JOURNAL OF

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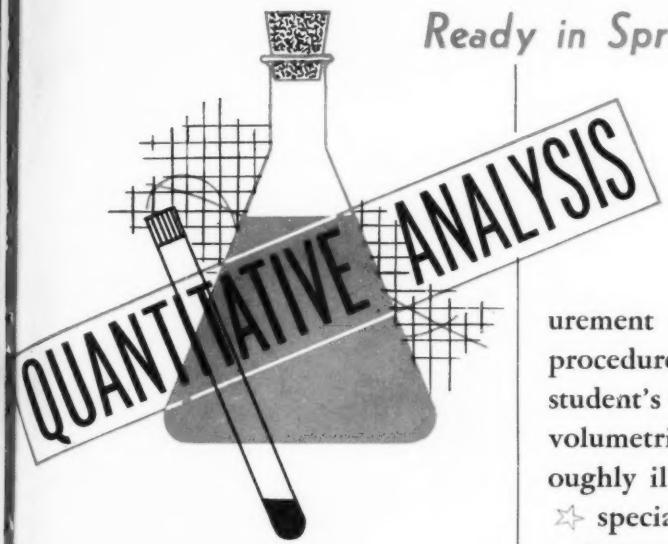

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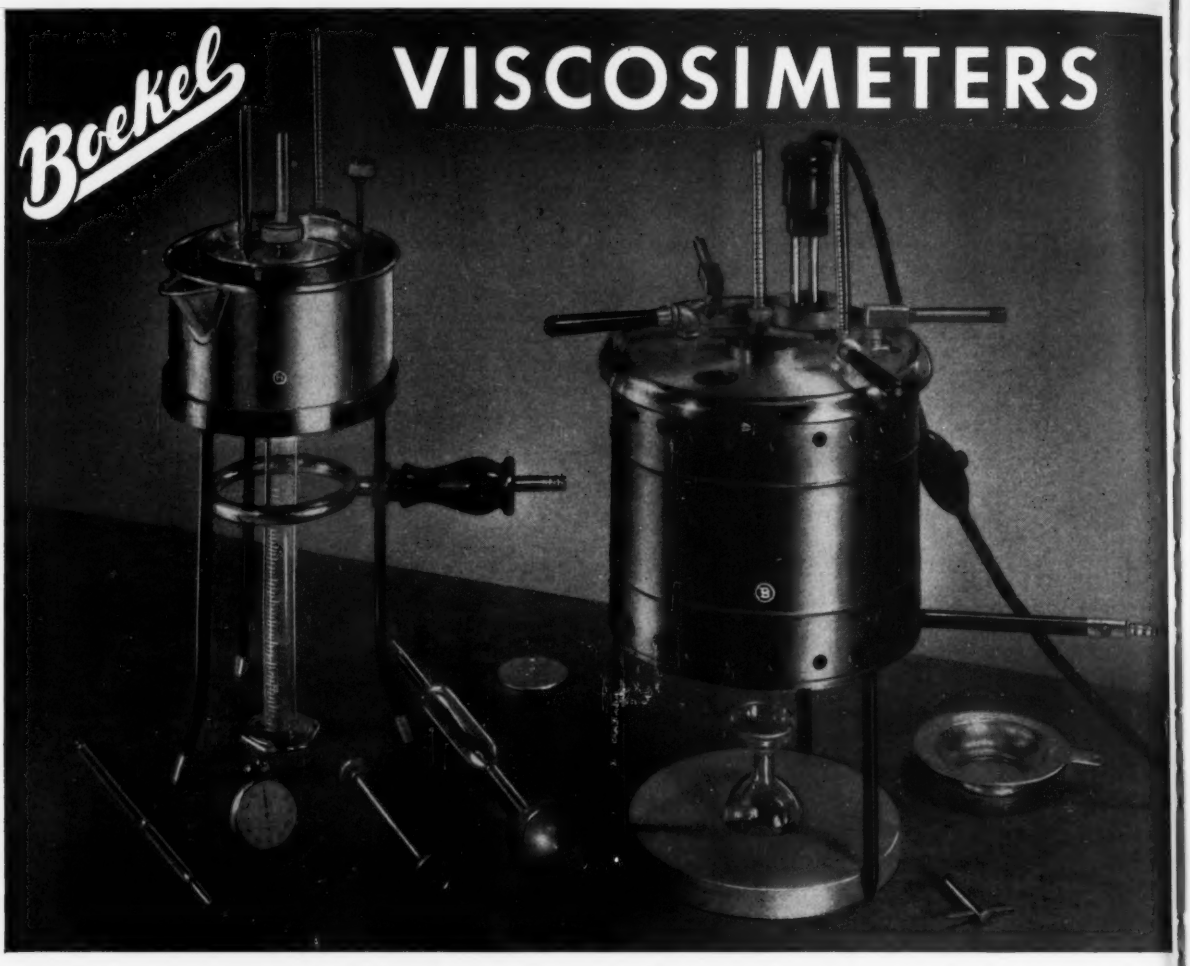

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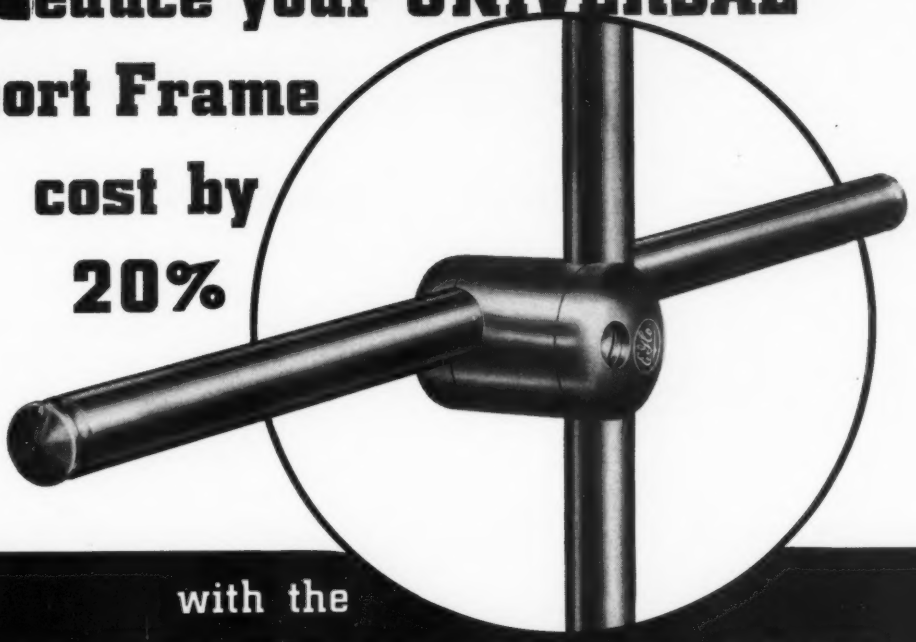

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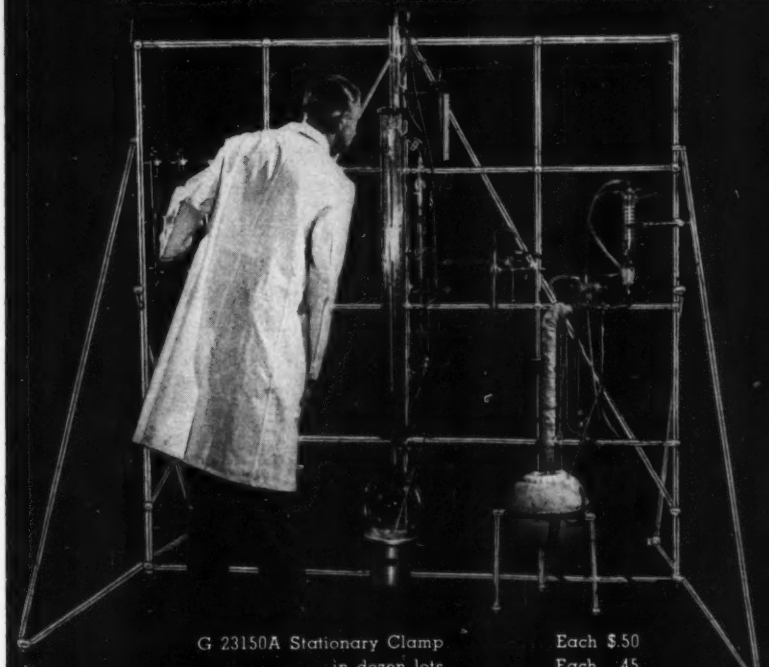

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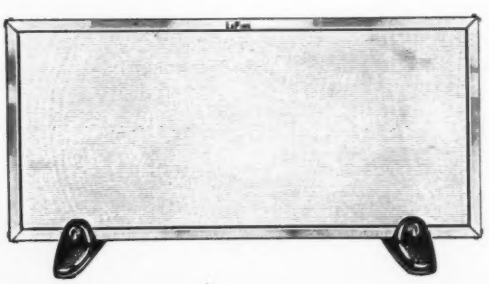

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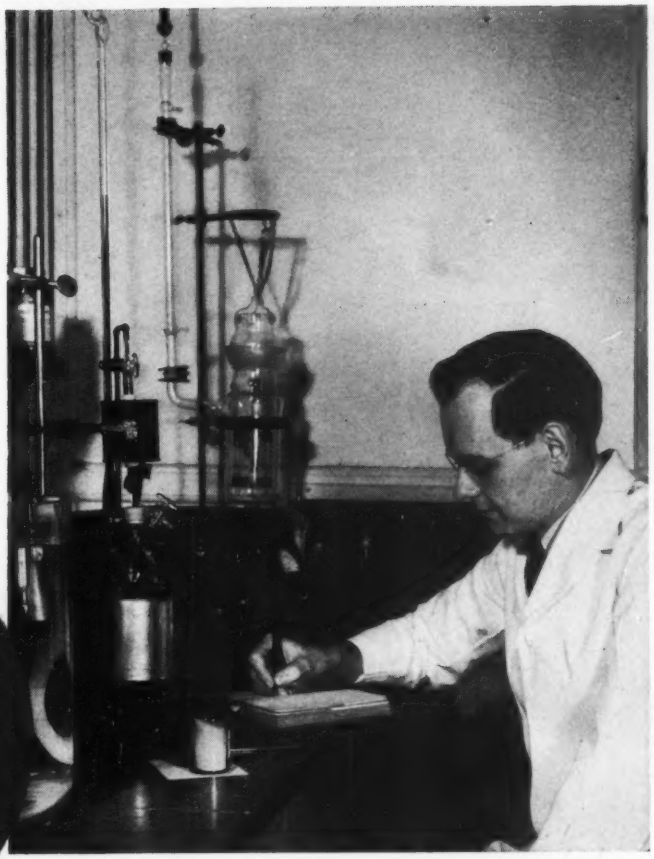

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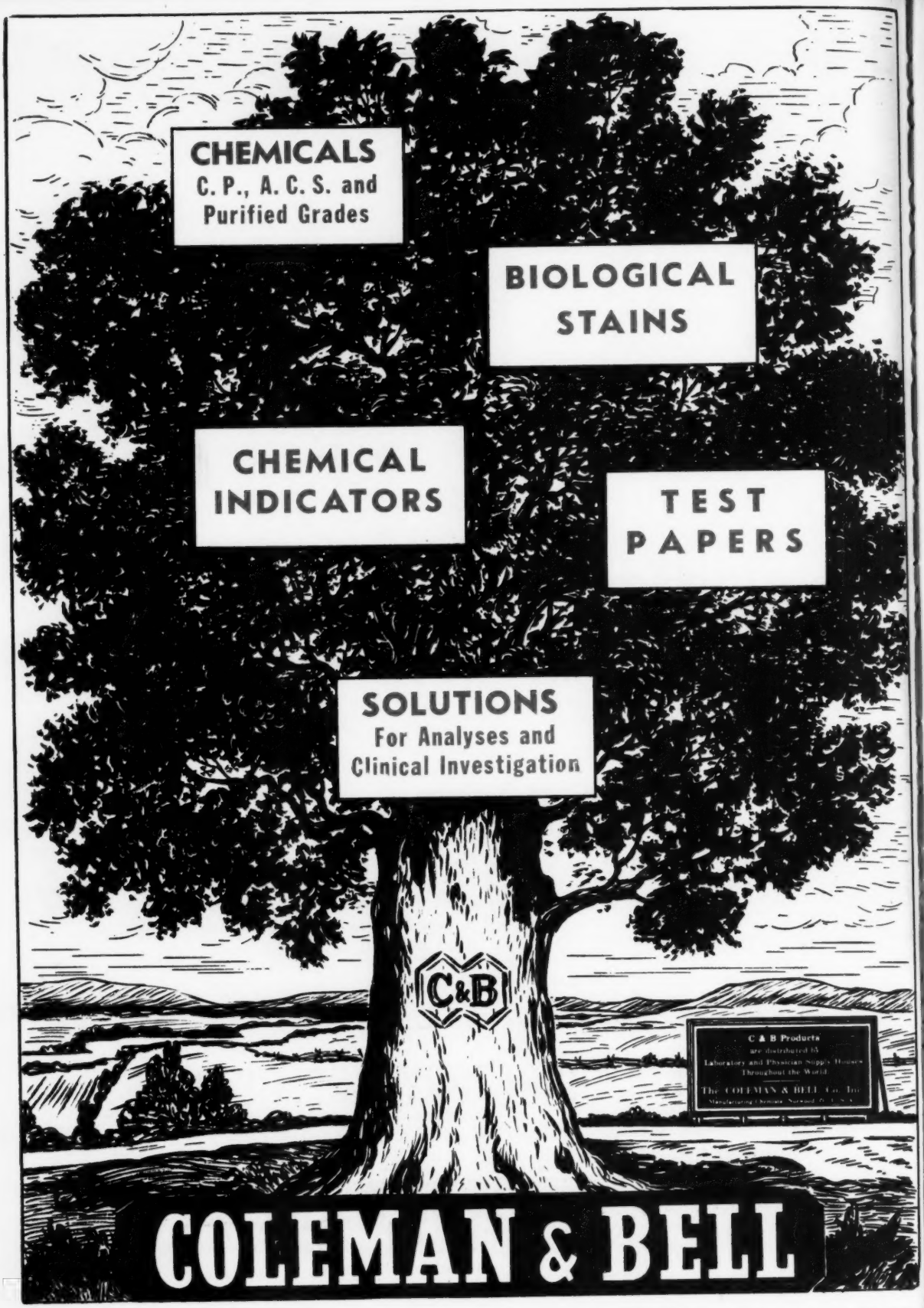
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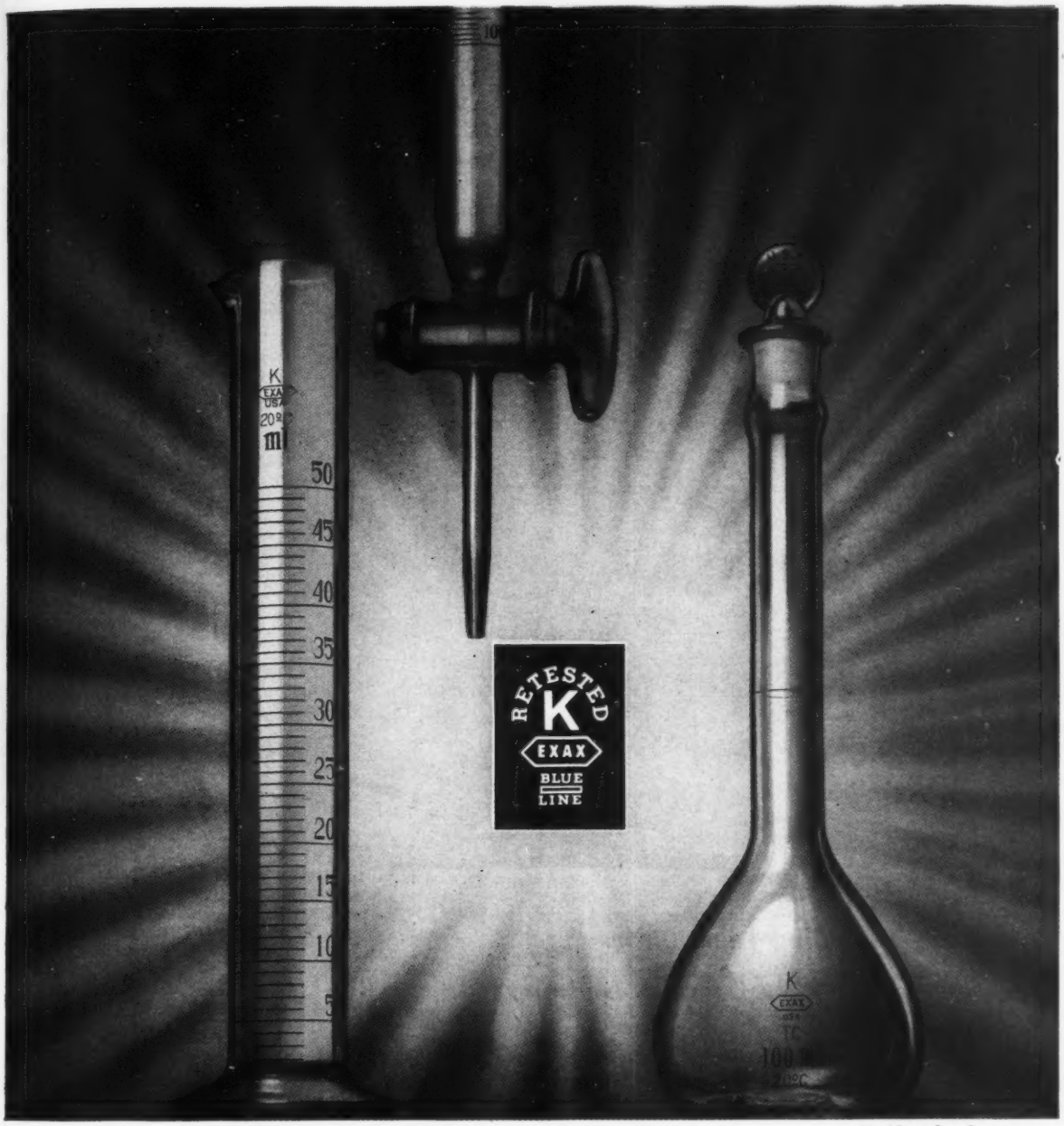

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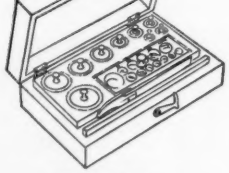

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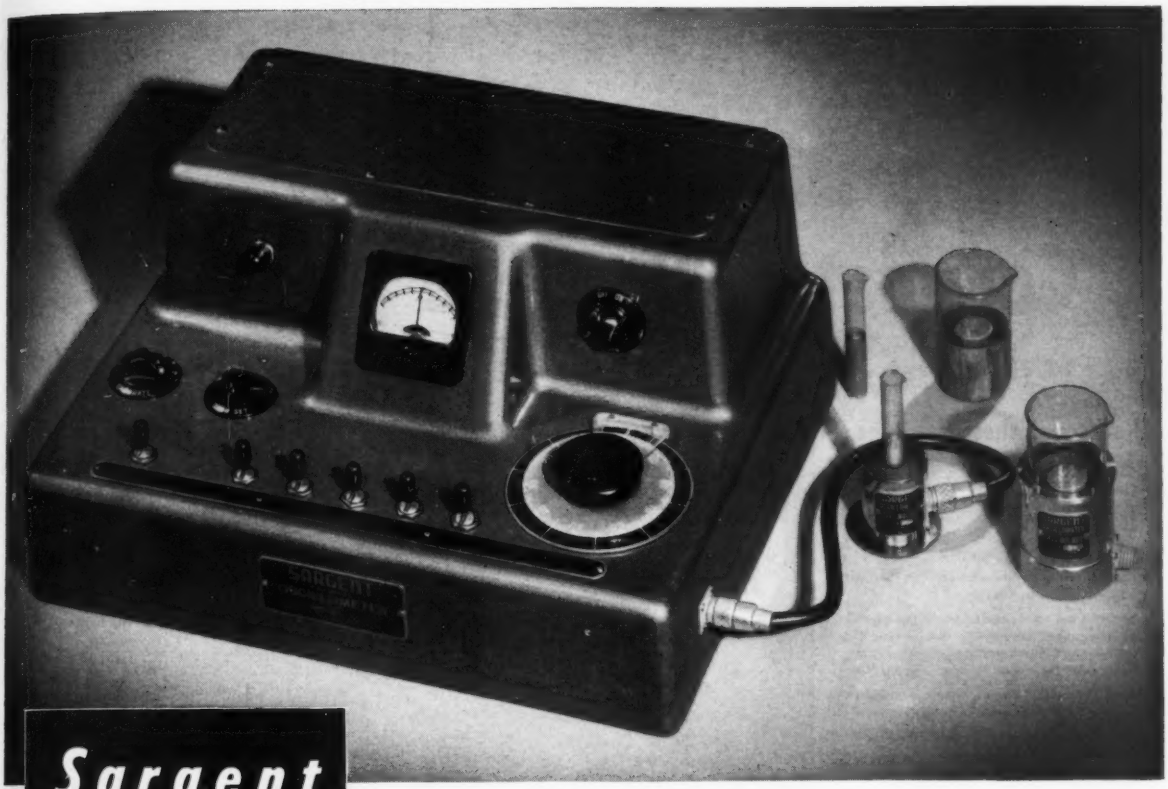

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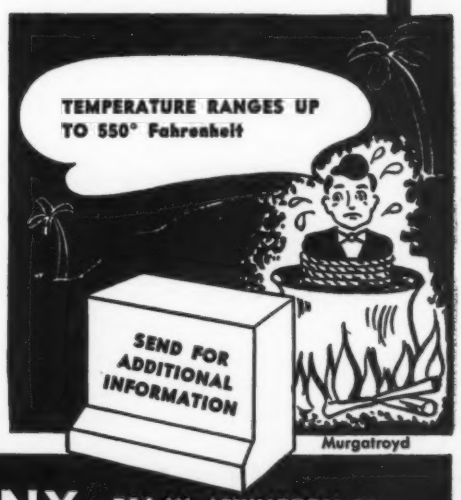

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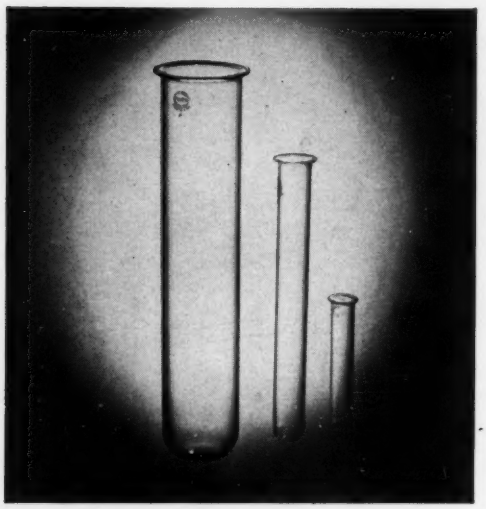

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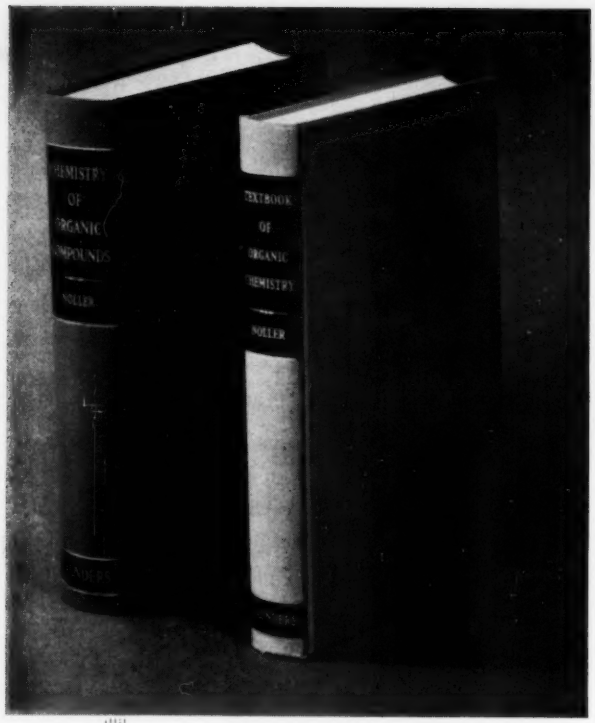

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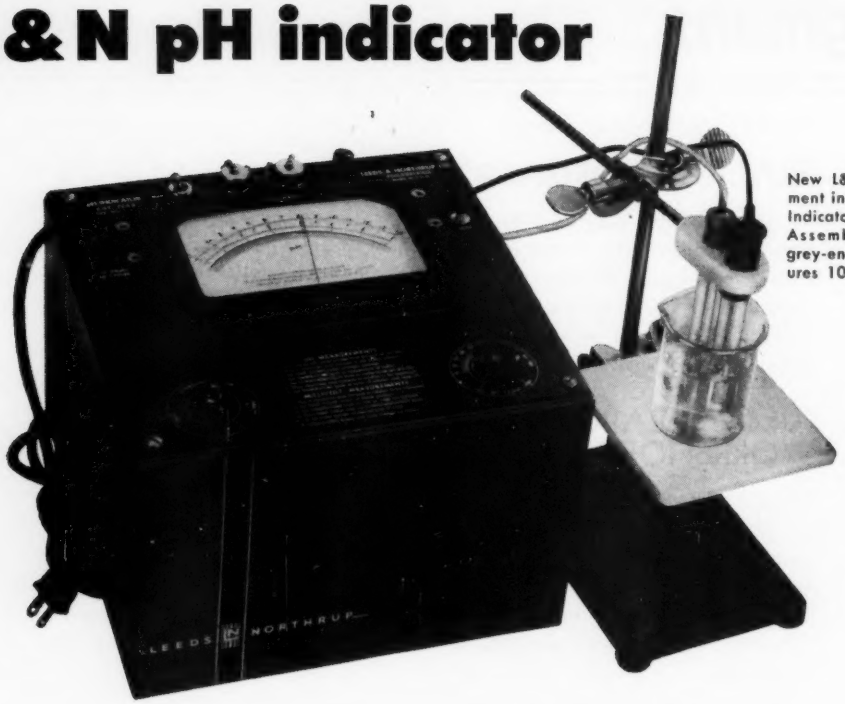

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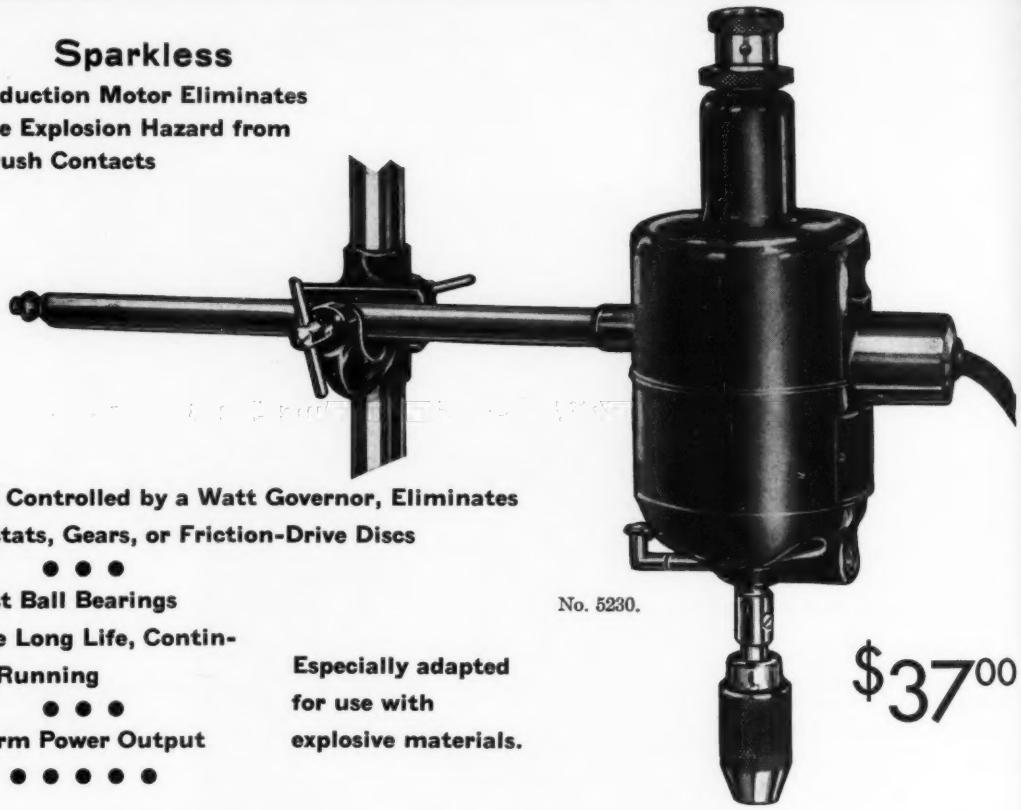

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Editor's Outlook

THIS number leads off with an unusual article which requires some comment and explanation. Written by several members of the Russian Academy of Sciences and evidently inspired from some still higher source, it lays down the "line" for consideration of the theory of resonance which it attacks so vigorously. The existence of this paper, in the original, has been referred to several times in the scientific and popular press, but we think it is such a remarkable document that it should be published in English where chemists in general can read it. Its significance, for chemists all over the world as well as in Russia, will be apparent; we need point no moral. It can well serve as a basis for many a lesson in scientific philosophy: what is the nature and the proper function of a theory, how shall a theory be regarded, when shall it be discarded and why?

While the resonance theory of the structure of organic compounds is generally accepted as useful, at least by chemists in this country, still there are many conscientious objectors, some of whom will doubtless raise their objections on what will be considered sound scientific grounds. In publishing this article we do not believe we are furnishing such objectors with any very strong weapons.

For those who may wish to read a short summary of the purpose and content of this article before plying into the details, we suggest the first two paragraphs of section III, on page 4, and the last paragraph in this section, at the bottom of page 8.

Following this article, on page 13, have been added some sections from another article with the same purpose as the preceding but without such official prestige. These excerpts indicate, perhaps even more clearly, the basis of this whole attack.

We are greatly indebted to Dr. Irving Bengelsdorf for making this material available in English.

THE PRESENT STATE OF THE CHEMICAL STRUCTURAL THEORY[1]

D. N. KURSANOV, M. G. GONIKBERG, B. N. DUBININ, M. I. KABACHNIK, E. D. KAVERZNEVA, E. N. PRILEZHAEVA, N. D. SOKOLOV, and R. Kh. FREIDLINA[2]

(Translated[3] *by Irving S. Bengelsdorf,*[4] *University of Chicago, Chicago, Illinois)*

THE second half of the nineteenth century was marked by the greatest event in the history of organic chemistry—the creation of the chemical structural theory by the Russian scientific genius Aleksandr Mikhaĭlovich Butlerov. This theory from the moment of its origin, and throughout its entire subsequent development has been and still is the firm foundation of all organic chemistry and the sure guide for all the researches of organic chemists. The creation of the structural theory led to an exceptionally rapid and vigorous efflorescence of organic chemistry, and to the development of organic chemical industry indissolubly connected with such growth.

The essential content of Butlerov's teaching is the assertion that the chemical structure of molecules is real, and that the chemical properties and mutual relations of compounds are caused by their chemical structures. Butlerov wrote: "Starting with the idea that each of the component chemical atoms of a compound participates in the formation of the latter, and there exerts a definite and specific quantity of chemical force (affinity), I designate as *chemical structure* the distribution of the action of this force by which the chemical atoms, indirectly or directly influencing one another, are united into a chemical particle" (*1*). And further: "If, at the present time, we attempt to determine the chemical structure of a substance, and if we succeed in expressing that structure in our formulas, then such formulas will (to a certain though imperfect degree) be rational formulas. In this sense, only one rational formula is possible for each compound, and, when the general laws governing the dependence of chemical properties on chemical structure have been derived, this formula will express all of these properties" (*2*).

Butlerov's concept of chemical structure, as given above, proves indisputably that he is the actual and sole author of the structural theory, and that his views differ sharply from those of Kekulé and Couper, who saw in structural formulas only the reaction formulas of compounds or the means of systematizing such substances. Kekulé's thought was expressed in the following words: "Just which of the different rational formulas is to be used in particular cases is essentially a question of the purpose pursued. The grounds for the assumption of different rational formulas for one and the same compound cannot be discussed on the basis of present-day concepts. Of course, it should be kept in mind that the *rational formulas* are *only reaction formulas and are not structural formulas* [underlined by Kekulé—Authors[5]]. They are nothing but expressions for the reactions of substances and for the comparison of various substances with one another; by no means can they express constitution, that is, the relative positions of the atoms in the corresponding compounds" (*3*).

The role of Butlerov in the creation of the structural theory is characterized by the great Mendeleev as follows: "Butlerov, by his study of chemical reactions, seeks to penetrate to its very depth the nature of the bonds which firmly unite the various elements into one whole; he recognizes that each of these elements has the inherent capacity to enter into a certain number of compounds; and he attributes the different properties of these compounds to differences in the method of bonding the elements. These ideas had not previously been developed so consistently by anyone, although they had vaguely appeared earlier. However, they appeared either as the fragmentary account given by Couper, or as the views of a number of scientists (*e. g.*, Kolbe) who wished to ignore Gerhardt, and as the expressions of men like Kekulé, who, believing in no theoretical concept at all, considered the subject solely from the point of view of systematics" (*4*).

[1] Report of the Commission of the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R., for the investigation of the present state of the theory of chemical structure; approved for publication by the Scientific Council of the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R.

The Bureau of the Division of Chemical Sciences of the Academy of Sciences, U.S.S.R., has deemed it desirable that further discussion of this problem be transferred to the pages of the journals, *Izvestiya Akademii Nauk S.S.S.R. Otdelenie Khimicheskikh Nauk* (*Bulletin of the Academy of Sciences U.S.S.R., Division of Chemical Sciences*), *Zhurnal Fizicheskoĭ Khimii* (*Journal of Physical Chemistry*), and *Zhurnal Obshcheĭ Khimii* (*Journal of General Chemistry*).

[2] Translator's note: The transliteration of all Russian names in this article is in accord with the current usage of *Chemical Abstracts*.

[3] From *Uspekhi Khimii* (*Progress of Chemistry*), 19, 529–44 (1950).

[4] Present address: California Institute of Technology, Pasadena, California.

[5] Translator's note: In the copy of Kekulé's book which was consulted (see literature cited) only the words "rational formulas" are italicized.

The structural formulas suggested by Couper and nowadays accepted in organic chemistry afford a good method of depicting chemical structures. It would, however, be entirely incorrect to equate the idea of chemical structure with the method of writing structural formulas. As the preceding citations show, the idea of chemical structure is much broader and deeper than the idea of the sequence and multiplicity of the bonds between the atoms in the molecules depicted by structural formulas. Butlerov, himself, attached no decisive significance to the method of writing structural formulas, thinking, "What matters is not the form but the essence, the concept, the idea" (*1*).

Many scientists, however (among them regrettably also certain Soviet scientists) do not comprehend the full depth of the Butlerov idea of chemical structure; they reduce it to a scheme for writing structural formulas. These scientists, of course, perceive neither the true function of the structural theory in the development of organic chemistry nor the great role of its creator, Aleksandr Mikhaĭlovich Butlerov.

The structural theory, in the 90 years of its existence —from Butlerov's day to ours—has followed a complex path of development. This development has been brought about by surmounting the many contradictions which have come to light during the investigation of organic compounds and their mutual relations. One very important contradiction of this kind was the discrepancy between the number of possible isomers predicted at the time by the structural theory, and the number actually discovered. In some instances, the number of isomers found was greater than the number predicted by the theory; this situation led to the origin and development of stereochemistry. In other instances the discrepancy was in the other direction; and this fact led to the (recognition of the) phenomenon of tautomerism. It should be noted that Butlerov was also the first to state not only the idea of the spatial arrangement of atoms in molecules but also the idea of reversible isomerization at equilibrium.

In the earlier stages of the development of the structural theory there were formulated the "law of residues or radicals" and the "law of type reactions." The first of these characterized the stability (*i. e.*, the invariance) of parts of the molecules (particularly their carbon skeletons) in chemical reactions. However, experimental investigations revealed the completely relative nature of this law. Numerous rearrangements conflicting with it were discovered; and the concept of the immutability of radicals was supplanted by a concept describing their stability and variability. In the development of the doctrine of rearrangements, Russian scientists played a prominent role. Here should be named A. M. Butlerov, V. V. Markovnikov, E. E. Vagner, A. I. El'tekov, N. Ya. Dem'yanov, A. E. Favorskiĭ, N. M. Kizhner, S. S. Nametkin, and others.

The law of type reactions required that a definite set of chemical properties (established by experiment) should correspond to each functional group—that is, to each structural element of the molecule. But experimental investigation also showed the completely relative nature of this law. It was Butlerov, and later on particularly his outstanding student V. V. Markovnikov, who created the doctrine of the mutual influence of atoms in molecules. In this theory it was shown that the type reactions of each functional group, that is, each structural element in the molecule, are not invariant. How completely they are manifested and what are their specific properties depend on the character of all the atoms in the molecule, even of those not immediately attached to the functional group in question; moreover, these manifestations in reactions depend on the number, mutual relations, and character of the bonds, etc.—that is, in the last analysis, on the chemical structure of the molecule as a whole. However, the nature and mechanism of the mutual influence of atoms on one another was inexplicable in Markovnikov's day, and his problem has been for many years (even up to our times) an outstanding problem in theoretical organic chemistry.

The introduction of the concepts of multiple bonds, aromatic properties, and conjugated systems, as well as the discovery of free radicals and many other such changes were great events in the development of the structural theory. They often necessitated changes and improvements in the concept of chemical structure. Occasionally, they required the repudiation of certain firmly rooted and universally adopted theoretical notions, *e. g.*, the notion that carbon in organic compounds is always tetravalent.

The structural theory, thus developed by the surmounting of contradictions, has always rested on Butlerov's basic ideas about chemical structure. The remarkable works of the prominent Russian chemists V. V. Markovnikov, A. M. Zaĭtsev, M. I. Konovalov, N. D. Zelinskiĭ, N. Ya. Dem'yanov, N. M. Kizhner, L. A. Chugaev, A. E. Favorskiĭ, A. N. Bakh, and many others have contributed greatly to the development of this theory. Moreover, structural theory has served as the scientific basis for industrial organic chemistry, the development of which, in turn, has enriched the theory. The structural theory, in the course of its development, has been transformed into a unique and harmonious theoretical system embracing all organic chemistry. It has an unsurpassed power to predict the possible types of chemical compounds, isomer numbers, and the chemical properties of organic substances. This structural theory, based on and firmly relying upon experiment, is deeply materialistic; it faithfully reflects the laws of organic chemistry which exist objectively and are dialectic in their nature.

II

At the end of the sixties of the last century, Dmitriĭ Ivanovich Mendeleev made the most significant discovery in the history of science, the periodic law of the chemical elements. In place of a chaos with an indefinite number of diverse and independent chemical elements, there appeared an orderly system reflecting the dialectic unity of these elements. The entire

subsequent development of chemistry and physics has been guided by an ever-deepening understanding of the essence of Mendeleev's periodic law. On the basis of this law and the discovery of the electron (end of the nineteenth century) there have been developed a theory of the structure of the atom and a theory of valence. This period is characterized by the first attempts to use electronic concepts in chemistry. Among the pioneers in this movement were L. V. Pisarzhevskiĭ, Ya. I. Mikhaĭlenko, and M. Berkengeĭm, the last of whom most consistently developed the applications of electronics to organic chemistry. Further development of electronic concepts in organic chemistry has been based on the current theory of electrovalent and covalent bonds. The physical foundation for this theory is supplied by quantum mechanics.

It is characteristic of the last three decades that, in this period, physical methods of investigating compounds have steadily penetrated deeper and deeper into organic chemistry. It cannot be said that organic chemists did not even earlier use physical methods for investigating organic substances. However, in the early stages, the determination of physical properties played only an auxiliary part in the researches of chemists. The chief purposes of such determinations were to identify compounds or to confirm the conclusions reached by chemical research. In the new stage, investigation by physical methods has acquired ever greater significance as a means of determining the structures of molecules—in the narrow sense of that term. That is, it is a means of determining the positions of atoms in space (valence angles, interatomic distances, etc.). It is also used to determine the polarities of individual bonds and of the molecule as a whole, the frequencies of vibrations, and many other properties.

At the same time that organic chemistry was permeated by physical methods of investigation the subject was also infiltrated by new concepts created by the progress of experimental and theoretical physics in the twentieth century. One of the most important of these is the concept of valence electrons responsible for the realization of the chemical bond. Chemistry originated and developed the concept that the covalent bond is formed by a pair of valence electrons. This concept was in turn borrowed by the physicists, and in this way, by mutual influence and permeation, the current theory of the chemical bond was created. Thus the remarkable prediction of the great Lomonosov was vindicated. He wrote, "These two sciences are so united that, without the other, neither can exist to perfection" (*5*).

The characteristic peculiarity of the present stage in the development of chemical structural theory is the permeation of this theory by quantum physics and quantum chemistry—most of all by Pauli's principle and the corpuscle-wave concept of the nature of the electron, a concept which has become the basis of contemporary scientific views on the nature of the chemical bond and the structure of matter. This present stage is an important step toward that understanding of the "general laws governing the dependence of chemical properties of bodies on chemical structure" about which Butlerov wrote.

III

The decisions of the Central Committee of VKP(b)[6] in regard to ideological problems and the sessions of the VASKhNIL[7] have mobilized Soviet scientists for the solution of the problem of a critical analysis of the present state of theoretical concepts in all fields of knowledge and the struggle against the alien reactionary ideas of bourgeois science.

The crisis of bourgeois science (connected with the general crisis of the capitalistic system) has manifested itself in the theoretical concepts of organic chemistry now being developed by bourgeois scientists. These have led to the appearance of methodologically faulty concepts which are slowing down further scientific development.

Characteristic, for bourgeois chemists, are an insufficient appreciation, as well as an incomplete understanding and a perversion of the Butlerov theory of structure. They replace Butlerov's concept of chemical structure by the structural formulas themselves. The theory of chemical structure is interpreted in a purely formal and entirely non-Butlerovian spirit; in fact, the name of Butlerov as the creator of the structural theory is usually not mentioned at all. This tendency is observed in almost all of the works of bourgeois organic chemists (books of Meyer-Jacobson, Richter-Anschütz, Holleman, J. Schmidt, Karrer, and the Fiesers). A statement by Hückel in his famous work, "The Theoretical Basis of Organic Chemistry" may serve as a striking illustration of the formal interpretation and the perversion of the true sense of the chemical structural theory. "Introduction of the methane type into mixed types led to the concept of the coupling of like atoms. This concept was expressed more clearly in the Couperian method of writing formulas than it was in the formulation by types. Hence the Couperian formulas soon supplanted the other less convenient formulas such as those of Kekulé and Loschmidt. According to this scheme, each atom in the molecule has a number of dashes corresponding to its valence number; and all the dashes of all the atoms in the molecule must be joined to one another; none may be free. In order to present this idea visually, the concept of hooks on the atoms was borrowed from the atomic theory. When atoms are joined, two hooks are coupled and are represented by a dash" (*6*).

The insufficiently appreciative and formal treatment of the Butlerov theory of chemical structure is equally manifest in works dedicated to special problems concerning chemical bonds and the structure of molecules.

[6] Translator's note: Vsesoyuznaya Kommunisticheskaya Partiya (Bol'sheviki). All-Union Communist Party (Bolsheviks).

[7] Translator's note: Vsesoyuznaya Akademiya Sel'sko-Khozyaistvennykh Nauk Imeni Lenina. All-Union Lenin Academy of Agricultural Sciences.

Thus, in Stuart's book, "The Structure of Molecules," there is not a word about Butlerov's theory. The newest books on the theory of organic chemistry, those of Pauling, Wheland, Branch, and others, suffer from the same general defect. Here too, the structural theory is only formally interpreted, and the name of Butlerov is not mentioned at all.

Thus the true idea contained in Butlerov's theory of structure is being perverted, and the materialistic concept of chemical structure (as an objective reality) is being replaced by formal schemes which clear the way for idealistic concepts. At the same time, there occurs a tendentious falsification of historical facts, the essence of which is the belittlement of the importance of Russian science.

The utterances of bourgeois scientists are also characterized by features of philosophic pragmatism. Thus, Pauling has the following definition of the chemical bond and of the molecule: "We shall say that there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species" ((7), p. 15, English ed., p. 3). In this treatment the objective criterion of the reality of the molecule and of the chemical bond vanishes. Since the definition of the molecule and of the chemical bond given by Pauling is methodologically incorrect, it naturally leads, when logically developed, to absurd results.

In a number of other places in Pauling's book, the "convenience" of the use of some concept is likewise regarded as a sufficient basis for the introduction of that concept into science (7) (for example, p. 22).

In the twentieth century, the basic defects of bourgeois thought in the field of natural science are a "physical" idealism and (particularly) a mathematical fetishism. "Reactionary aspirations are being bred by the progress of science itself. The wide advance of the natural sciences, the approach to uniform and simple elements of matter, the laws of motion which can be mathematically treated produce the oblivion of matter by mathematicians. 'Matter disappears,' equations alone remain. At this new stage of development, and in a quasi-novel fashion there reoccurs the old Kantian idea that the mind orders the laws of nature" (V. I. Lenin, Volume 14, p. 294, 4th ed.).

In theoretical chemistry this "physical" idealism is particularly evident in the theory of resonance developed by Pauling, Wheland, and some of their followers. In this theory, on the basis of a formal interpretation of one of the possible methods for the approximate calculation of molecules, there has been created a concept of "quantum-mechanical resonance structures" (as though it existed as a physical phenomenon); this is then widely used for the "explanation" of real facts and relationships. This is done in the following manner: The wave function Ψ (which describes the state of the molecule) is approximately represented by a sum, to each member of which is ascribed the meaning of a definite chemical structure. It is then asserted that the "resonance" of these "structures" causes the real state of the molecule.

Thus a new concept of so-called "resonance structures" is introduced into chemistry. These structures are considered as though they existed; in the words of the theory of resonance, in each molecule they "are in a state of superposition." All the properties of the molecule and even the fact of its existence are predetermined by the character of these resonance structures and their superposition. Thus "resonance structures" and the resonance between them are the chief "discovery" of the theory of resonance.

Careful consideration of the resonance theory shows that there is no actual basis for the introduction of "resonance structures" into science. This concept is connected, as pointed out above, with a particular mode of interpreting the separate wave functions, the linear combination of which serves as the approximate mathematical description of the state of the molecule. If other approximate methods of calculation are used, "resonance structures" and "resonance" do not arise at all.[8]

As shown by the above discussion, the basic assertion of the resonance theory that "resonance" in some way can determine the properties of molecules is devoid of meaning. The entire immense body of factual material at the disposal of organic chemistry gives no reason to suspect, even in a single instance, that resonance structures exist or that there is any resonance between them. Hence, to introduce into science the concepts of "resonance structures" and their "resonance" has neither experimental nor theoretical justification. This fact is a striking example of the estrangement of idealistic theory from practice.

Evidently, the lack of foundation of the principles of the resonance theory is recognized by its author, Pauling. This conclusion follows from the fact that, in his reasoning, he attempts to build under this theory at least the semblance of an experimental basis. However, as is well known, chemistry does not confirm the fundamental tenets of the resonance theory. Therefore, Pauling takes the stand that methods for detecting resonance structures do not yet exist. In his book, "The Nature of the Chemical Bond," he writes, "The difficulty for benzene and for other molecules showing electronic resonance is to devise an experimental test which could be carried out quickly enough and which would distinguish among the structures under discussion" ((7), p. 413, English ed., p. 429). This quotation shows that in Pauling's opinion resonance structures and resonance have an objective existence. As a matter of fact, however, neither the separate resonating struc-

[8] We do not here consider the question whether the separate components of the function Ψ have, in general, any physical sense, and if so what that sense is. This question is treated in our present literature (see, for example the article by N. D. Sokolov) (8).

tures nor resonance exists in the molecule. It is perfectly clear that the problem of isolating Pauling's resonance structures is senseless.

From what has been said, it follows that the concepts introduced into science by the idea that resonance structures are physical phenomena are also fictitious. Among these is (for example) the notion of "resonance energy"—a certain specific energy with its source in the "quantum-mechanical resonance structures." For many organic compounds there is a deviation between the experimentally determined energy of formation and the corresponding energy calculated according to the additive scheme; this energy Pauling identifies with the energy of "quantum-mechanical resonance." In reality, however, these deviations from additivity can obviously never be caused by the nonexistent resonance structures.

Pecularities in the reactivities of certain chemical compounds are also "explained" according to the theory of resonance as being due to the presence of resonance structures in the respective molecules. Pauling announces that the chief purpose of his theory is to derive the properties of a real molecule from the "properties" of these structures. Thus, for instance, he writes ((*7*), p. 45, English ed., p. 36): "Whenever a question arises as to the properties expected for a covalent bond with partial ionic character, it is to be answered by consideration of the corresponding resonating structures." On page 216 (English ed., p. 217): "From the new point of view the phenomenon of conjugation is attributed to resonance between the ordinary structures and certain structures involving one less double bond. . . ." On page 133 (English ed., p. 130): "The stereochemical properties of the benzene molecule can be predicted from the concept of resonance between the two Kekulé structures." Many similar examples might be cited from Pauling's book as well as from the books of his students and followers. In all these works, "resonance". . . "leads to," "explains," "causes," etc., certain properties of organic molecules.

Thus, Pauling and his followers substitute for the real molecule a collection of resonance structures, and for the actual factors which determine the properties of molecules a nonexistent resonance between these structures. Characteristically, foreign authors of books on the theory of resonance, and particularly Wheland (*9*), hold idealistic Machian views. They consider resonance to be a "theoretical concept," and subsequently they establish the "influence" of this resonance (*i. e.*, of this concept) upon the properties of the molecules (p. 49). Such views are known to be fairly widespread among bourgeois scientists.

The theory of resonance, in so far as it rests upon a methodologically false foundation, is undoubtedly a brake upon the further development of knowledge concerning chemical structure. Consistent use of the theory of resonance leads to pseudo-scientific conclusions and produces the semblance of a "scientific" explanation where essentially no explanation is given. Thus, the resonance theory hinders the creation of a more general and quantitative theory of organic chemistry. This conclusion is by no means refuted by the fact that many important and correct conclusions accepted in present-day theoretical organic chemistry were originally formulated in the language of the resonance theory. It is quite wrong to suppose that all quantum-mechanical calculations about molecules are a prerogative of the resonance theory. In reality, that theory can lay claim only to the incorrect interpretation of such calculations.

The theory of resonance, owing to its illusory ability to "explain" many facts incomprehensible to the organic chemist, has been widely accepted. In particular, C. K. Ingold, who shares the views of Pauling almost completely, agrees with this theory. In this connection, it should be observed that even before the formulation of Pauling's theory of resonance, Ingold, in an attempt to explain the mesomeric effect (phenomenon of mesomerism, see part IV of this article), thought it necessary to find for that effect a special quantum-mechanical source of energy which he called "the energy of perturbation." As a matter of fact, this concept is identical with the concept of the "energy of resonance." Ingold writes: "Thus, the specific and exclusive source of the energy required to determine the independence of the mesomeric effect is identified as the energy of 'perturbation' depending upon a degeneracy." And further: "The theory of electronic degeneracy in conjugate systems was independently developed in the works of Pauling... Pauling succeeded in evolving a method of treatment which, in principle, permits a comparative calculation of the energies of perturbation of conjugated unsaturated hydrocarbons. The phenomenon thus described is called by Pauling 'resonance'" (*10*).

Thus, the explanation of the phenomenon of mesomerism given by Ingold coincides with Pauling's concept of resonance. Similar statements may also be made about Eistert (*11*), Wheland (*9*) (pp. 12–17), and many others who use the term "mesomerism" in the same sense.

Thus, we see that antiscientific idealistic concepts are very prominent in the theoretical ideas now being developed by bourgeois scientists in the field of organic chemistry. The bourgeois chemical literature is choked with books which pervert A. M. Butlerov's theory of chemical structure and direct its further progress along a false path.

It is regrettable that the faulty concepts of bourgeois science have also exerted an influence upon certain Soviet scientists. This influence is expressed, first of all, by an insufficient understanding and appreciation of the true content of Butlerov's structural theory. Thus, in the foreword to the book by Ya. K. Syrkin and M. E. Dyatkina, "The Chemical Bond and the Structure of Molecules," is the statement: "Instead of the formal structural theory of the nineteenth century or the primitive electrostatic concepts of the beginning of the twentieth century, we have at our disposal a more perfect physical theory which can serve as the point of departure for the further successful development of the theory of the chemical bond and of molecular structure" (*12*). And

further, on page 56: "The ideas of the structural theory are exceedingly simple. It is sufficient to attribute one valence line to hydrogen, two to oxygen, three to nitrogen, and four to carbon; virtually all the experimental material of organic chemistry is embraced by this scheme."

Such a presentation of the structural theory has nothing in common with the true content of that theory. This fact is not surprising; in the book referred to, the name of Butlerov is not once mentioned. This perversion of the essence of the theory of structure, and the ignoring of the name of its creator, is totally impermissible on the part of Soviet scientists.

It should also be noted that certain Soviet scientists reproduce in their statements the perverted system of concepts belonging to the authors of the theory of resonance. In this respect, the book of Ya. K. Syrkin and M. E. Dyatkina "The Chemical Bond and the Structure of Molecules" may serve as an example.

At several points in this book, the authors correctly indicate that the resonance structures do not actually exist in molecules. They write on page 73: "In reality, there is but one cloud in the molecule, and its resolution into three structures is nothing but an appeal to more simple forms." However, on page 105, the authors write: "Consequently, both structures exist in each molecule. When the different structures are superimposed, there is formed a transitional structure which here plays an essential part, as it does in the hydrogen molecule, by causing a lowering of the energy, *i. e.*, a stabilization of the system." In this way the authors here consider the "resonance of structures" to be a physical phenomenon. The very large number of examples of this kind in the book by Syrkin and Dyatkina attests the uncritical approach of these authors to the theory of resonance, their inconsistency, and the contradictions in their treatment of the most important problem in chemical theory. Moreover, the entire spirit of the book is permeated by ideas belonging to the theory of resonance. This theory is here offered as the last word of science, as the theory called upon to solve almost all the unsolved problems of organic chemistry.

The authors, as a logical consequence of their erroneous views, still further aggravate the defects in the theory of resonance by carrying out an "account and isolation of the transitional structure," which Pauling "left out of consideration" (p. 248). The only reason for introducing a transitional structure is the fact that, in the square of the binomial expression $(\Psi_a + \Psi_b)$ there appears the term $2\Psi_a\Psi_b$.

In spite of the profound errors in the book by Ya. K. Syrkin and M. E. Dyatkina, "The Chemical Bond and the Structure of Molecules," this book was permitted as a textbook in chemical colleges. In this way, it aided in spreading the perverse idealistic theory of resonance among workers in the field of chemistry.

Analogous errors appear also in the book by A. I. Kipriyanov, "Electronic Theory in Organic Chemistry." He writes: "By using the concepts of resonance and of the stabilizing effect of resonance on complex molecules, it has been possible to explain, at least qualitatively, some properties of unsaturated and aromatic compounds which had not previously been understood" (*13*) (p. 24). A. I. Kipriyanov throughout his entire book considers resonance structures to be phenomena, and asserts that such structures really exist. Thus on page 58: "The hydrogen bond is strengthened by the resonance between structures. . . "; on page 85: "They [the acid properties of phenol—Authors] are predetermined by the character of the resonance structures of the undissociated phenol. . .," etc.

Two statements by M. V. Vol'kenshtein may be cited as another example of theoretical inconsistency and an uncritical attitude toward the resonance theory. One (the correct one) occurs on pages 57–8 of his book (*14*): "In reality, of course, there is no resonance; the electrons in the molecules are in completely determinate states which, in principle, can be ascertained without discussing the states of free atoms and without mentioning the purely speculative states Ψ_i and Ψ_k or the corresponding energies ϵ_i and ϵ_k. The second (the incorrect one) appears on page 106: ". . . the actual state of the molecule is the result of a superimposition of the individual structures, just as the state of an individual bond is the result of a superimposition of a homopolar and an ionic bond."

A series of further erroneous statements by other Soviet authors might also be cited. In these, the resonance of structures is regarded as a specific quantum-mechanical phenomenon. Particularly, in a series of papers by S. I. Lur'e (recently published in the *Journal of General Chemistry* under the general title "Investigations on the application of the theory of resonance to the chemistry of organic compounds") (*15*) the faulty concept of the resonance of structures as a physical phenomenon is supplemented by completely arbitrary considerations regarding the mechanism of chemical reactions.

It should be noted that public opinion among the scientists of the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R., did not attend to the disclosure of the defects of the resonance theory at the proper time. Furthermore, a number of the workers in the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R. (including some of the authors of the present article) have regarded the theory of resonance uncritically and have used it in some of their previous papers. Cases of this sort which merit particular reference are the employment of the resonance theory to explain the properties of quasi-complex compounds (A. N. Nesmeyanov, R. Kh. Freĭdlina) (*16*), of organometallic derivatives of anthracene (B. M. Mikhaĭlov) (*17*), and of aromatic ethers (D. N. Kursanov) (*18*), as well as to explain the peculiarities of the combination scattering spectra of ethylene derivatives (E. N. Prilezhaeva) (*19*). There is also an uncritical attitude toward the theory of resonance in the lecture course which M. I. Kabachnik gave for aspirants[9] in the Institute of Organic Chemistry, and

[9] Translator's note: graduate students.

in the review which he published in the journal *Uspekhi Khimii* (*Progress of Chemistry*) (*20*).[10]

In many respects, work on the present article has helped its authors critically to review their ideas on the problem of the resonance theory, and has aided them to make more precise and to deepen their views on all the other problems here touched upon. Those authors in whose works errors and inaccuracies with respect to these problems have been permitted, will reckon it their duty to correct such errors in subsequent publications.

Until recently, criticism of the resonance theory by Soviet scientists did not reveal the basic methodological defects of that theory. Statements adverse to the resonance theory which were made by individual chemists were either directed against particular errors in that theory (V. N. Ufimtsev) or were made on false grounds (G. V. Chelintsev). Nevertheless, these statements played a certain positive role; they helped to fix the general attention of Soviet scientists on the necessity for a critical analysis of the resonance theory.[12]

G. V. Chelintsev's views on the theory of resonance are expressed in his book (*21*). There, the author justly criticizes the definition of the chemical bond and of the molecule given by Pauling. But the basic methodological defect of the resonance theory—its "physical" idealism (see above)—is not mentioned in Chelintsev's book.

It is essential to note that G. V. Chelintsev incorrectly identifies the theory of resonance with the entire contemporary theory of chemical structure; hence his criticism of the resonance theory is mostly directed not against that theory, but against all modern views about chemical structure. On the other hand, the application of wave mechanics and the introduction of its concepts into theoretical chemistry has further developed Butlerov's theory and made it more concrete (see below). One of the principal points in G. M. Chelintsev's criticism of the theory is his denial of the possibility that bonds may be delocalized.[13] This view is in contradiction to firmly established experimental facts; it distracts attention from actual criticism of the resonance theory.

Evidently, to comprehend the nature of the chemical bond one must apply and take into account all the data of present-day chemistry and physics. In the "New Structural Theory" proposed by G. B. Chelintsev, an attempt is made to construct a new theory of the chemical bond without taking these data into account. Chelintsev "simply" postulates in a very nebulous way that there exist only two types of chemical bond, "orbital" and "contact." By means of this innovation alone, he attempts to explain all the phenomena and regularities of organic chemistry. One of the postulates of his theory is that, in any polyatomic molecule, each pair of valence electrons is "localized" either within a single atom ("contact bond"), or between at most two atoms ("orbital bond"); that is, each pair of electrons, independently of the other electrons, moves along a one- or two-electron orbit. This type of localization of electrons in definite "orbits" is, of course, incompatible with their wave properties.

A theory built on incorrect basic assumptions naturally comes into conflict with experimental facts. Thus, for example, G. V. Chelintsev's "contact formula" for benzene contradicts the presence of a symmetry center and the equivalence of the carbon atoms in the benzene molecule. Similarly, according to G. V. Chelintsev, the molecules of ethylene, butadiene, naphthalene, anthracene, and phenanthrene should have dipole moments, whereas actually they do not. It is easy to multiply the number of examples which show that the "new structural theory" is inconsistent with generally known facts. A number of Soviet chemists have repeatedly called G. V. Chelintsev's attention to these and many other unavoidable contradictions between the basic facts of physics and chemistry on the one hand and his postulates with their consequences on the other. It is significant that even the author himself does not apply his "new structural theory" in his writings. This theory should be rejected.

Thus, until recently Soviet organic chemists had made no sound and poignant Party criticism of the idealistic concepts of bourgeois scientists in the field of organic chemical theory. It is urgently necessary to develop such criticism on the basis of Marxian-Leninist methodology, and in so doing to use all the achievements of present-day chemical science.

[10] In this article the Editorial Board has inserted a note[11] the incorrect and baseless character of which was acknowledged in the speech of the responsible Editor, speaking in the name of the Editorial Board during the discussion at the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R., Feb. 7, 1950.—Editorial Board.

[11] Translator's note: The note referred to above was inserted by the Editorial Board into Kabachnik's 1948 review article on "Orientation in the benzene ring." The translation of the note is as follows:

"The Editorial Board deems it necessary to make the following remarks on the correlation of the resonance theory with the theory of electronic displacements. A chemist, no doubt, has the right to use some of the visual concepts of the latter theory. In so doing, he is justified not only by the extremely complex apparatus of the resonance theory, but also by the fact that this theory meets with many essential difficulties when the attempt is made to use it for the solution of concrete chemical problems. But although these theories are correlated, they cannot, in principle, be equivalent. On the contrary, one of them rests on the most general achievements of natural science, whereas the other is still a collection of artificial *ad hoc* models and mechanisms. Thus, when the attempt is made to bring the language and concepts of the two theories into mutual correspondence, the proper approach is as follows: those tenets of the theory of electronic displacements which can be made to correspond to the language of the resonance theory have the right to remain in the arsenal of chemical methods; those tenets, however, which can be shown to contradict the language of the resonance theory must be excluded from that arsenal.—Editorial Board."

[12] Since the present article was discussed in meetings of the Scientific Council of the Institute of Organic Chemistry of the Academy of Sciences, U.S.S.R., on Feb. 3–7, 1950, articles by V. M. Tatevskiĭ and M. I. Shakhparanov, by O. A. Reutov, and by V. M. Tatevskiĭ have appeared in the press (*28*); these articles are omitted from the present discussion.

[13] Concerning the delocalization of bonds, see part IV.

IV

One of the most important problems of theoretical organic chemistry is that of the mutual influence of the atoms in molecules. As early as 1861, A. M. Butlerov, in his formulation of the basic ideas of the structural theory, pointed out that the concept of chemical structure includes the mutual influence of all the atoms in the molecule (see part I).

The further development of the doctrine of the mutual influence of atoms is the achievement of Butlerov's outstanding student V. V. Markovnikov, who demonstrated the exceptional importance of this problem. In 1869, Markovnikov, in his famous dissertation entitled "Data on the Problem of the Mutual Influence of Atoms in Chemical Compounds" (*22*) wrote: "The problem of the influence of elementary atoms on the direction of the chemical reactions of a complex substance is among the most intriguing problems of contemporary chemistry. As already stated, it occupies more and more of the attention of chemists. This problem was destined to arise naturally as soon as the majority of chemists had assimilated the doctrine of chemical structure, for it is the direct continuation and further development of that doctrine."

V. V. Markovnikov, like Butlerov, points out that "the character of the elements in a compound is determined not only by the elements directly bound to them, but also by those which are held in the same chemical system with them by some polyatomic element." (*22*). Guided by the notion of the mutual influence of atoms, Markovnikov studied various reactions of substitution, addition, and dissociation. The famous "Rules" which bear his name generalize the experimental results which he obtained. Markovnikov understood his "Rules" not as isolated regularities of organic chemistry but as particular manifestations of a general law the discovery of which he foresaw. "Once a certain store of facts has been obtained, it is possible to generalize and thus to predetermine the course of the reactions of a given limited group of compounds. But the time will come when these generalizations will merge into a single general law; and the direction of our investigations which is still more or less empirical will then change and it will be replaced by one based on strictly defined laws of the conversion of substances."

In the subsequent development of organic chemistry, the mutual influences of atoms and groups of atoms in molecules were found to be subject to numerous regularities. These were expressed in the appropriate and well-known rules of organic chemistry, for example the rules of orientation in substitution and addition reactions. The discovery of these rules made it necessary still further to develop and to amplify the theory of chemical structure. In this connection, one should note M. A. Il'inskiĭ's ideas with regard to the possibility of splitting valences (*23*), L. A. Chugaev's theory on the nature of complex compounds and their analogy to organic compounds (*24*), A. M. Berkengeĭm's (*25*) theory of the electronic structure of organic compounds, and many others.

In 1913 V. A. Izmail'skiĭ (*26*) in his studies on color found certain facts concerning the mutual influence of atoms in the molecules of some organic dyestuffs. These facts were of such a nature that the chemical structures of the dyestuffs could not be expressed unambiguously by any conventional structural formula. At the same time, it was perfectly clear that the dyestuffs studied were individual substances and that they consequently had a definite chemical structure.

The organic chemistry of the first two decades of the twentieth century is characterized by the accumulation of a considerable number of facts showing the mutual influence of atoms to be of such a nature that the actual structure of certain substances could not be described with sufficient accuracy by any conventional structural formula. Examples of this type have been shown to be specially abundant among aromatic compounds and compounds with conjugated double bonds. Investigation of the structure of these compounds has enabled chemists to penetrate more deeply into the essence and the mechanism of the mutual influence of atoms.

This same period is also characterized by the fact that at this time electronic concepts made their way into organic chemistry. The original object of the electronic theory in this field was to give an electronic interpretation of the chemical bonds in structural formulas. This stage of the development is noteworthy for new and important advances: discovery of the part played by electron pairs in the formation of various sorts of covalent bond; determination of the nature of the semipolar bond; explanation of the polarity of the covalent bond; etc. At a later stage, an attempt was made to interpret electronically the nature and the mechanism of the mutual influence of atoms and groups of atoms in molecules; also, the construction of a theory of reactivity was begun. Here the electronic interpretation was based on the theory of electron displacements. This theory in turn involved the positions (in Mendeleev's periodic system) of the elements composing the molecule. Following Markovnikov, the effect of any atom in a molecule was evaluated by comparing the properties of a given substance with those of another compound in the molecules of which the place of the atom under consideration was occupied by a hydrogen atom. Various types and mechanisms of mutual atomic influence in molecules were systematized. The present state of the problem appears to the authors to be as follows.

The mutual influence of atoms in a molecule can be propagated along an atomic chain in at least two ways. One of these, called the induction mechanism, is the characteristic form of propagation for σ-bonds. Here the observable mutual influence of two atoms not directly connected with one another grows rapidly weaker as the number of intervening atoms is increased. This phenomenon may conceivably be caused by a deformation (displacement) of the electron cloud of the

σ-bond which occurs when new substituents or new structural elements are introduced into the molecule, or when the molecule is subjected to the action of an external field.

The other method for the propagation of mutual atomic influence is characteristic for groups with π-bonds, especially for those with conjugated bonds; it is called the "tautomeric mechanism." "Tautomeric" influences, unlike inductive influences, extend throughout the length of the conjugated chain. This phenomenon may be caused by the fact that electron clouds can be considerably more deformed when they occur in π-bonds than when they occur in σ-bonds. Consequently, in a system of conjugated π-bonds, there is a characteristic and more or less far-reaching equalization of the density of the π-electrons along the entire chain of conjugation; and hence the polarizability of the system is increased.

It may be regarded as established that both of the mechanisms just discussed can be operative in a nonreacting molecule (so-called "static" effects) as well as at the moment of a chemical reaction ("dynamic effects"). Under the latter circumstances, the direction and the extent of the displacement of electron density are determined not only by the chemical structure of the molecule under consideration, but also by the character of the attacking reagent.

The above sketch gives only a very general outline of the problem. Soviet chemists and physicists should collaborate intensively to develop a theory of the mutual influence of the atoms in the molecule. Here special attention should be paid to uprooting the remnants of the influence of the resonance theory.

In the chemical literature the distribution of the electron density in a nonreacting molecule has been called the state of polarization (extent of polarization) of that molecule, and until recently the term polarizability has been applied only to a qualitative description of the distribution of the electron density under the action of an external field, or under the action of an attacking molecule at the moment of chemical reaction.

Progress in the investigation of the mutual influence of atoms has made it possible to form a more complete idea of the chemical structure of those substances the structures of which are poorly represented by structural formulas of the conventional type. This class of substances is composed principally of aromatic compounds and compounds with conjugated bonds. It has been found that, in molecules with conjugated bonds, the density of the electron cloud is distributed in a way which does not correspond to the distribution of the density when isolated single and multiple bonds are present. This phenomenon has been called, not very fortunately, the "delocalization of bonds." In some instances (higher polyenes, naphthalene, etc.) delocalization causes a very considerable equalization of the bonds. In the extreme case (benzene), all the C—C bonds are equivalent and the valence states of all the carbon atoms are identical.

Such peculiarities of chemical structure, particularly in compounds with conjugated systems of bonds or aromatic nuclei, manifest themselves by heats of formation higher than those calculated according to the additive scheme, and also by the specific deviations of a number of other physical constants. These same peculiarities of chemical structure are also very clearly revealed by certain chemical properties, for instance by the specific properties of aromatic compounds. A remarkable property of compounds containing conjugated systems is that, although these substances have no tendency to tautomerize, they react in two ways. Here, the reaction center is moved along the chain of conjugation.

The concept of the conjugation of simple (σ) bonds as well as the conjugation of simple bonds with multiple bonds is now being developed by Soviet chemists. This constitutes a further advance in the theory of the mutual influence of atoms in organic compounds.

Early in the thirties the first systematic treatment of electronic displacements was suggested by Ingold. He subdivided them into the following "effects": inductive (static induction), mesomeric (static tautomeric), inductomeric (dynamic induction), and electromeric (dynamic tautomeric). In the chemical literature, the manifestation of the mesomeric effect has been called mesomerism.

It has already been pointed out that the explanation of mesomerism given in the works of Ingold, Eistert, Wheland, and many others coincides with Pauling's concept of resonance. It is clear from the account given here that the manifestation of the mesomeric effect as one of the forms of the mutual influence of atoms in molecules can by no means be regarded as identical with the nonexistent resonance of structures.

It seems to the authors that the very term "mesomerism," which has been widely interpreted in the spirit of resonance, might advantageously be replaced by some more precise term which has never been perverted by association with resonance structures.

It should be noted that, in the minds of chemists, the term mesomerism is usually connected with a structure of an intermediate character. This idea should be understood as follows. Actually, when an organic chemist finds the mutual influence of atoms and groups of atoms to be manifested in characteristic chemical and physical properties, he rightfully compares the properties of atoms and groups of atoms in the compound under consideration with the properties of the same atoms and groups of atoms in structurally related compounds. From the differences between these properties, it is inferred that the distribution of electron density in the atom groups under consideration is intermediate with respect to the distribution of electron density in the corresponding atom groups of the compounds used for comparison.

Thus, for example, the properties of the nitro group in nitrobenzene differ from the properties of the nitro group in aliphatic nitro-compounds on the one hand, and from the properties of the nitro group in the *p*-nitrophenol ion on the other. Again, the properties of

the benzene ring in nitrobenzene differ from the properties of the benzene ring in benzene and from the properties of the benzene ring in the *p*-nitrophenol anion (quinoid type). It is precisely in this sense that one may speak of the intermediate nature of the atom group under discussion. However, the concept just described (which is actually used by organic chemists and which was proposed by A. N. Nesmeyanov (*29*)) differs sharply from the concept of intermediate chemical structure as developed by Arndt (*27*), Ingold (*10*), Wheland (*9*), and others who compare the real molecule with fictitious "saturated," "unexcited," etc. (essentially "resonance") structures.

The systematization introduced by Ingold (and by Robinson) has played a certain positive role inasmuch as it started the development of the current electron theory of the reactivity of organic compounds. However, the explanations given by members of the English Chemical School (including Ingold) were connected with the methodologically false concepts already described. Hence they could not lead to a correct understanding of the mutual influence of atoms in a molecule.

It should be noted that the Ingold systematization, even if supplemented by the idea of the conjugation of a double bond with an ordinary C—H bond, is still largely insufficient, since it is far from accounting for the diversity of the manifestations of the mutual influence of atoms in molecules. In particular, this scheme of systematization does not account for all the chemistry of free radicals nor for homolytic reactions (reactions which are accompanied by the splitting of electron pairs).

Since the terms of the electron theory have been interpreted in various ways by large groups of organic chemists, it is necessary, in critically examining the literature published during the last 10 to 15 years, to pay sharp attention and to distinguish the correct statements (based on experimental material, on the idea of the mutual influence of atoms, and on other correct propositions) from incorrect interpretations (based on the tenets of the resonance theory).

It was pointed out above that ordinary structural formulas are not always adequate to express the idea of chemical structure in its Butlerovian depth. In particular, the mutual influence of atoms in the molecule, especially of those which are not directly connected with one another, is not reflected by structural formulas alone. There is at present no fully satisfactory method of representing molecules so as to reflect either the influence of atoms or (more important) the structure of activated complexes. Two methods have been suggested: (1) equipping the usual structural formulas with arrows to show the direction of electron displacements, and (2) using a set of structural formulas. Each of these methods has its advantages and its deficiencies. The principal deficiency of the first is that its descriptive possibilities are limited. The chief disadvantage of the second is that its use may suggest the idea that the molecule is polystructural in character, whereas in reality every molecule has just one definite structure. The consideration just mentioned shows that a corresponding amount of discretion will be necessary from now on when sets of structural formulas are used for purposes of description.

It ought to be especially stressed that it is necessary to devise a single method of representing molecular structures which will depict the mutual influences of atoms and will closely correspond to objective reality.

At the time when electron concepts in organic chemistry had been partially formulated, quantum mechanics made its appearance and was applied to the solution of chemical problems. A physical interpretation was found for D. I. Mendeleev's Periodic Law and for the valences of the elements. A quantum-mechanical theory of the covalent chemical bond was devised, and the most remarkable property of this bond, its saturated character, was explained. The idea of a bonding pair of electrons, which had been previously developed by chemists, was confirmed. Quantum mechanics made it possible to give a qualitative treatment of directed valence and of the stereochemistry of atoms in their various valence states.

The calculations used in quantum mechanics, despite their approximate character, reveal that the idea of the delocalization of bonds in aromatic and conjugated systems (which had previously been elaborated by chemists on the basis of experimental findings) agrees with the basic principles of contemporary physics. The founding of the theory of the transitional state (activated complex) in chemical reactions (theory of absolute reaction velocities) should also be noted. The qualitative conclusions reached by means of this theory have been applied in organic chemistry.

It should be emphasized that most of the approximate calculations regarding organic molecules (provided that they are made by some method which, from the point of view of quantum mechanics, can be justified) quantitatively characterize the chemical structure of these molecules and take into account the mutual effects of their component atoms. These calculations, despite their approximate character, may play a positive part in theoretical organic chemistry.

A. M. Butlerov's theory of chemical structure enriched by the results of quantum physics is now sufficiently developed to permit it to undertake the solution of numerous difficult and important problems in organic chemistry. Aromatic carbocyclic and heterocyclic compounds have been successfully treated. The idea of nucleophilic, electrophilic, and radical reagents has been used as the foundation for a theory of the reactivity of organic compounds. The foundation for a theory of substitution in the benzene ring has also been laid. A qualitative explanation has been found for the regularities which Markovnikov expressed in his Rules, and for the exceptions to these rules which are covered by the rules of Zaĭtsev and Krasuskiĭ. A qualitative explanation has been given for the lability of hydrogen and other atoms in organic compounds; this lability depends on structural factors and on the nature of the substituents. Moreover, the relation between the peculiar

properties of aromatic and conjugated systems and their planar structure has been qualitatively explained; for example, the differences between the chemical properties of benzene and those of cyclo-octatetraene have been accounted for. New types of steric hindrance (suppression of the mutual effects of substituents in the benzene ring when these substituents are forced out of the plane of the ring) have been predicted and found. A deeper penetration into the interdependence between many physical properties and chemical structure has been attained.

But theoretical organic chemistry, at its present stage of development, still badly fails to account for many known facts and relationships. Even today the electron theory is still essentially qualitative, and this fact limits its applicability when the problem under consideration has a marked quantitative aspect. Many experimentally established regularities among saturated compounds have not yet been theoretically explained. The theory of reactivity which involves the division of reagents into the nucleophilic, electrophilic, and radical classes is still in many respects insufficient. The problems connected with the structure of an activated complex (transitional state in chemical reactions) have scarcely been touched. The problem of explaining theoretically the effect of the medium on the reactivity of organic compounds is also still in its initial state.

Soviet chemists have made fundamental contributions to the theory of chemical structure. The researches of N. D. Zelinskiĭ and his students especially on organic catalysis and on the chemistry and contact reactions of hydrocarbons; of A. E. Favorskiĭ and his students on acetylene and its derivatives; of S. V. Lebedev on polymerization; of A. N. Bakh on biochemistry; of P. P. Shorygin on high molecular and organometallic compounds; of L. A. Chugaev on complex compounds and terpenes; of N. Ya. Dem'yanov and M. N. Kizhner on alicyclic compounds; of A. P. Orekhov on alkaloids; of A. E. Porai-Koshits on dyestuffs—these and many others are the pride of Soviet organic chemistry and of international chemical science.

The high traditions of Russian organic chemistry are now being maintained by Soviet organic chemists who form an army many thousand strong. The aim of Soviet chemists in the field of organic chemical theory is to develop and perfect the Butlerov theory of chemical structure, by overcoming the defects of the contemporary electronic theory and creating a more general and quantitative electronic theory of organic chemistry. Here one important objective is a general solution of the Markovnikov problem (that is the problem of the connection between the chemical structure and the physical properties of organic compounds) and the construction of a more perfect theory of organic chemical reactions.

In theoretical organic chemistry the problem before Soviet chemists is to generalize the voluminous experience gained by the Soviet organic chemical industry and all those branches of industry served by organic chemistry, and to use the results obtained by the theory in every way which may help to solve the practical problems in the establishment of Communism in our country.

There is no doubt that Soviet chemists educated in the great traditions of the Russian chemical science founded by Lomonosov, Butlerov, and Mendeleev, armed with the Marxist-Leninist world outlook, and guided by the great party of Lenin-Stalin will successfully attain the objectives before them.

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ABOUT A MACHISTIC THEORY IN CHEMISTRY AND ITS PROPAGANDISTS[1]

V. M. TATEVSKIĬ and M. I. SHAKHPARANOV
(*Translated by Irving S. Bengelsdorf*)

Editor's Note: Several extracts from the article of the above title are here published to accompany the preceding article. They are in the same vein and have the same purpose—condemnation of the theory of resonance as incompatible with the basis of Russian thinking. The aspect of this theory to which the Russians so violently object is revealed in the following quotation from Wheland's "Theory of Resonance and Its Application to Organic Chemistry":

"From the foregoing discussion we see that resonance is a man-made concept in a more fundamental sense than most other physical theories. It does not correspond to any intrinsic property of the molecule itself, but instead it is only a mathematical device, deliberately invented by the physicist or chemist for his own convenience."

It would seem that it is hence possible to draw a conclusion concerning the great scientific significance of this theory. However, a critical examination of it does not lead to such a conclusion. On the contrary, analysis shows that the physical content of the theory of resonance is erroneous and that the philosophical setting of its authors and propagandists is Machistic. The Machistic theoretico-perceptional settings of the theory of resonance can serve as one of the examples of those world outlooks hostile to the Marxist view. They lead bourgeois scientists and their followers to pseudo-scientific conclusions in the solution of concrete physical and chemical problems.

It is fully evident that the physical and philosophical bases of the theory of resonance are intimately connected one with another. It could be incorrectly thought that this theory is simply a collection of physical errors not connected with the methodological tenets of its creators. It would be just as incorrect to think that the perverse philosophical outlooks have no relationship to the concrete contents of the theory. The reactionary world outlook, the atmosphere of general decadence and decay of culture, of art, and of science in the perishing bourgeois society gives rise to various Machistic theories which have lost contact with practice and do not reflect objective reality. The theory of resonance is one of these theories.

Soviet society has the right to require a party approach to the exposition of scientific problems from our publishers and from our authors—who are Soviet scien-

[1] From *Voprosi Filosofii* (*Problems in Philosophy*), **3**, 176 (1949).

tists. This exposition must fully indicate, from the point of view of Soviet patriotism, the role of Soviet scientists in the elaboration of these or other scientific problems.

Directing the attention of Soviet chemists along the fallacious path of the vicious theory of resonance, the authors,[2] in this manner, demobilize Soviet chemical science in its struggle to fulfill the basic tasks of the Soviet scientists—"not only to attain, but to excel, in the shortest time, the achievement of science beyond the boundaries of our country" (Stalin).

Thus, it is quite obvious that Ya. K. Syrkin and M. E. Dyatkina have appeared before the Soviet public in the unenviable role of propagandists for the avowedly erroneous and vicious theory of the American chemist, Pauling.

Have Ya. K. Syrkin and M. E. Dyatkina exhausted their blunders? Unfortunately, no.

The State Scientific-Technical Publishing House, publishers of chemical literature, entrusted the translation and editing of the book by Linus Pauling[3] to Ya. K. Syrkin and M. E. Dyatkina.

It would have been natural to expect that the translator and editor of the book would consider the philosophical premises of L. Pauling, so that they could analyze the connection between the Machistic views of Pauling and the content of the resonance theory which he preaches.

Instead of that, Prof. Ya. K. Syrkin wrote a laudatory preface to Pauling's book. In this bulky volume there is not even one reference to the papers of Russian or Soviet scientists. One might have expected that the translator and editor, fighting for the honor of Soviet science, would have tried to fill this gap in the preface, and in the footnotes. In the preface, however, Prof. Ya. K. Syrkin does not mention a word about this. Moreover, the footnotes which Syrkin gives at the end of the book substantially represent references to papers of American and English chemists which Pauling omitted in his book.

Let us return to the book by G. W. Wheland,[4] which was edited by Ya. K. Syrkin and translated by M. E. Dyatkina in 1948. The philosophical positions of Wheland have already been characterized above. Wheland openly preaches a Machistic thesis of the speculativeness of physical theory.

Wheland, as a loyal servant of the reactionary bourgeoisie, does not mention a word, of course, about the papers of Soviet scientists. Among the numerous references to the papers of bourgeois scientists, Wheland, however, does not forget to cite the efforts of Chichibabin (who left and failed to return) and to cite the papers of the former White Guard Kistyakovskiĭ. In the preface to Wheland's book, Prof. Ya. K. Syrkin writes:

"Wheland's book suffers from a defect peculiar to many other books by American and English authors. Wheland ignores Soviet papers. And yet, however, Soviet scientists are responsible for substantial papers in theoretical organic chemistry. Numerous papers on these subjects can be found by the reader in the scientific-technical Soviet publications."

Permeated with a Machistic and cosmopolitanistic ideology, by a slavish uncritical attitude toward bourgeois science and a contemptuous attitude toward native science, the book by Ya. K. Syrkin and M. E. Dyatkina diverts Soviet chemistry from the solution of practical problems, in the direction of the bankrupt and sterile theory of resonance. The publication of this book, as well as Pauling's and Wheland's monographs, is a serious error committed by the publishers of chemical and foreign literature. The Ministry of Higher (University) Education, which has admitted the Machistic and cosmopolitanistic book by Ya. K. Syrkin and M. E. Dyatkina to serve as a study aid for the chemical faculties of the universities, has also committed a great error. An analysis of the theory of resonance demonstrates how carefully and critically one must approach not only the philosophical, but also the general theoretical principles of reactionary scientists in capitalistic countries, in all fields of science.

There is no doubt that progressive Soviet chemistry, by maintaining the glorious tradition of the great Russian chemists, Lomonosov, Mendeleev, Butlerov, and Markovnikov, and by leaning on the only scientific world outlook (the world outlook of Marx-Engels-Lenin-Stalin), by discarding and exposing the pseudo-scientific theories of bourgeois scientists, will attain, in the near future, new progress in the development of a theory of chemical structure and in the solution of the most important problems of theoretical chemistry.

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[2] Syrkin and Dyatkina ("The Chemical Bond and the Structure of Molecules")—Ed.

[3] PAULING, L., "The Nature of the Chemical Bond," State Scientific-Technical Publishers of Chemical Literature, Moscow-Leningrad, 1947.

[4] WHELAND, G. W., "The Theory of Resonance and Its Application to Organic Chemistry," State Publishing House of Foreign Literature, Moscow, 1948.

THE USE OF LIGHT SCATTERING FOR DETERMINING PARTICLE SIZE AND MOLECULAR WEIGHT AND SHAPE

MAX BENDER
American Cyanamid Company, Bound Brook, New Jersey

EVERYONE is familiar with the visible beam in a dark movie or vaudeville house or visible sun rays through clouds, especially on a hazy day. In both cases, the rays or beams are visible because of particles of dust and fog in their path, scattering the light. Since the particles are sufficiently large in size, and abundant, enough scattered light comes at an angle from the beam to the observer so that the path of the original beam can be followed.

The phenomenon of scattering is basically one of diffraction. However, at the larger particle sizes where the particle diameter is equal to and greater than the wave length(s) of the incident light, a definite proportion of the scattered light is the result of reflection also. Scattered light has, for the most part, the same wave length as the incident light and, therefore, cannot be explained as an ordinary fluorescence.

Light scattering has been used for quite some time to distinguish qualitatively between colloidal dispersions and "true" solutions (Faraday-Tyndall effect). Nevertheless, the present trend is to interpret quantitative values connected with the light itself in terms of molecular weight and shape. Useful information is obtained by measuring relative intensity, depolarization, and angular distribution of the scattered light, and analyzing these quantities in terms of the electromagnetic theory of radiation and the kinetic theory of matter.

The range of molecular or particle sizes over which such calculations have been applied is tremendous. At the small end of the scale, Cabannes checked Avogadro's number with calculations based on his (Cabannes') quantitative measurements of the intensity of light scattered by argon (*3*), and Debye and co-workers (*4*) checked the molecular weight of sugar in similar fashion. On the other end, weight and shape properties of particles as large as the wave length of light have been estimated.

Much work has been done with respect to the quantitative interpretation of the light scattered by solutions, but considerably more research is necessary with many systems before full and accurate information can be derived. For instance, the relationships and information now available on light scattering usually are based on the suspended matter's being in the iso-disperse state; yet most of the systems one is concerned with are hetero-dispersed and serious complexities are therefore introduced. Also, allowances must be made for solute concentration. The systems described in the literature are dilute. Often it would be more desirable to study the disperse phase at higher concentrations, but drastic modifications would probably have to be made in interpreting the measured properties of the scattered light. It is true that one could dilute a given suspension before examining it, but one is not then sure of how the state of aggregation has been affected thereby.

FARADAY-TYNDALL EFFECT

If the particles in suspension are at least of colloidal dimensions and the difference in refractive index between solute and solvent is sufficiently great, the path of a beam of light through the solution can be discerned without recourse to special technique, whereas it can hardly be seen in a true solution. This effect is known as the Faraday-Tyndall phenomenon named after Faraday and Tyndall, who first made use of this phenomenon in their researches. The Tyndall beam is diagrammed in Figure 1.

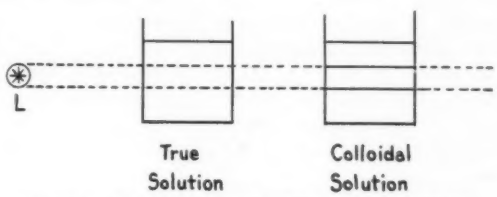

Figure 1. Path of the Tyndall Beam through Solutions

By observing certain collidal sols with the microscope as they exhibited the Faraday-Tyndall effect, Zsigmondy found that the *individual* particles of the sol were discernible through their halos even though they were too small to be actually resolved microscopically. He used this discovery to gain an insight of the size of colloidal particles. The procedure is indirect and the results obtained are rough, but this has been of great importance in furthering the knowledge about colloid systems. The concentration of particles was estimated by counting the halos in a given volume of the suspension illuminated at an angle of 90° to the line between the observer's eye and the suspension, and the weight of material in suspension per unit volume was determined by drying down the sol after dialysis to remove electrolytes. Then, with a knowledge of the density of the substance, Zsigmondy calculated the average radius of a particle, using the formula:

$$r = \left(\frac{3c}{4\pi ns}\right)^{1/3} \quad (1)$$

where r is the radius in cm., c is the grams of solute in 1 cc. of suspension, s is the density of the solute in grams per cc., and n is the number of particles per cc. Molecular weight M would be:

$$M = \frac{c}{n}N \quad (2)$$

where N = Avogadro's number, *i. e.*, 6.02×10^{23}.

The instrument developed by Zsigmondy for carrying out the measurement of n is known as the ultramicroscope. Light from a carbon arc is focused as a fine slit of given width and thickness in the sol which is contained in a cell on the stage of the microscope.

SMALL ISOTROPIC PARTICLES

Rayleigh Concept (3, 13, 17)

Lord Rayleigh pointed out in 1871 that light scattering by particles small compared with the wave length of light was basically a diffraction phenomenon and not caused by refraction, reflection, or fluorescence.

Upon encounter of an isotropic particle of sufficient optical density, with a beam of light, the electrons of the particle, being charged units, are caused by the incident electromagnetic impulse to vibrate in unison with it, an oscillating electric moment thus being induced in the particle. These oscillating electrons are the sources of the scattered (or diffracted) light which for the most part has the same frequency as the exciting wave.

Scattered light is given off from the particle at every angle and the incident beam is weakened in intensity accordingly. Since the vectors of the induced electric moments are parallel to those in the exciting beam, there will be variations in intensity of the scattered light, depending on the angle at which it emanates from the particle. One result is that the light scattered at right angles to the incident beam will be plane polarized irrespective of the state of polarization of the incident beam.

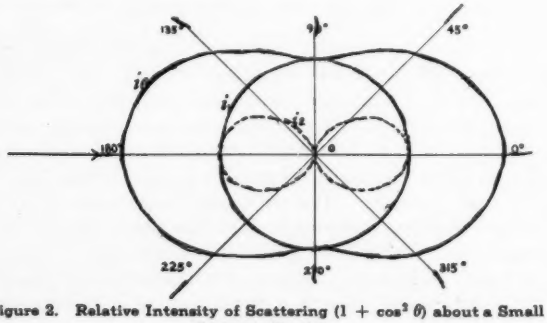

Figure 2. Relative Intensity of Scattering $(1 + \cos^2 \theta)$ about a Small Isotropic Particle

Rayleigh derived, mathematically, a relationship between the scattered proportion of the incident light, its wave length, the particle size, and the optical properties of the scattering suspension. It involved consideration of the electromagnetic moment (or polarization) resulting in the particle when exposed to the incident light, and expression of this in terms of refractive index by use of the relationship between polarization and the index of refraction. Equation (3) represents a form of this relationship. Note that the limitations are small isotropic spheres in dilute suspension, the radius being no greater than $^1/_{20}$ the wave length of the incident light. The incident light is unpolarized.

$$\frac{i_\theta}{I_0} = \frac{9\pi^2 n V^2}{2d^2(\lambda')^4}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2(1 + \cos^2\theta) \quad (3)$$

"i_θ" represents the intensity of that light energy scattered per unit volume of solution at a given angle θ with the proceeding incident beam (*i. e.*, the angle between the primary and the scattered or secondary beams being viewed), the intensity of the incident beam being I_0. "i_θ" may be designated by its components of polarization i_1 and i_2. "n" equals the number of particles per cc. and its inclusion in the formula gives the proportionate light scattering in terms of 1 cc. rather than one particle. "V" corresponds to the volume of a particle. Note that with this factor squared, the intensity of the scattered light is proportional to the sixth power of the radius of the particle. This shows the tremendous effect of particle size on light scattering and one can readily understand why it is essential in light-scattering experiments to eliminate all large extraneous particles like dust which scatter much light even though they are present in a relatively low concentration.

"m" is the ratio of the refractive index of the particles to that of the solvent. "d" is the distance between the observer and the scattering system and is simply the usual factor of spherical propagation of energy.

"λ'" represents the wave length of the light falling on the particles, *i. e.*, the wave length in the solvent medium. This is calculated from the wave length in vacuum (λ) by dividing λ by the refractive index (μ_0) of the solvent. Note that with λ' raised to the fourth power, the intensity of the scattered light will be markedly affected by the magnitude of the wave length and there will be much greater scattering (i_θ/I_0) of the shorter blue wave lengths as compared with the longer red wave lengths. It was by means of this relationship that Rayleigh was able to account for the blueness of the sky.

The term $(1 + \cos^2 \theta)$ defines the geometry of the range in which both components of the incident (unpolarized) light are scattered. "1," the unity term, pertains to the scattering (i_1) of that component of the incident light whose direction of vibration is perpendicular (or vertical) to the plane containing the illuminating source, the scattering particle and the observer's eye. It is propagated uniformly in all directions by the vibrating particle. The $\cos^2 \theta$ refers to the scattering (i_2) of the other component of polarization, whose direction of vibration is in the plane (horizontal component). It is seen that when θ is 90°, i_2 becomes zero.

Figure 2 illustrates the relative intensities of both components of polarization in the scattered light individually as well as combined. The particle is at the

origin 0 and the intensity of scattering at a given angle θ with the incident beam (I_0) is proportional to the straight line between 0 and the curves pertaining to the component(s). "i_1" is represented by the thin continuous curve and i_2 by the dotted curve. The heavy continuous curve pertains to i_1 plus i_2, namely i_θ.

The Debye Treatment

Highly Dilute System (*4, 7*). In determining molecular weight (M) for systems of small isotropic particles at high dilution, it is more convenient to work in terms of the attenuation of the incident beam by the scattering solution. This extinction due to scattering or turbidity (τ), as it is called, can either be directly measured or evaluated from scattered light intensity (*4*) and the need for considering d as included in equation (3) is thereby eliminated.

When light (of initial intensity I_0) passes through a medium in which particles of solute are in suspension, it will lose intensity depending on the degree of scattering. This can be set up in the form of an expression similar to that of Beer's law, *i. e.*:

$$\frac{-dI}{dx} = \tau I \qquad (4)$$

where x is the distance along the beam in the solution. The proportionality constant τ naturally depends on the number and size of the scatterers in the solution and therefore can be described on a similar basis as the Rayleigh concept. For the case of the light which is scattered at 90° with the incident beam, and which, as has already been pointed out, is plane polarized (*i. e.*, the $\cos^2\theta$ term in equation (3) is zero), τ is expressed by Debye (*4*) according to equation (5):

$$\tau = \frac{32\pi^3\mu_0^2(\mu - \mu_0)^2}{3}\frac{1}{\lambda^4}\frac{1}{n} \qquad (5)$$

where μ and μ_0 are respectively the indices of refraction for the solution and solvent. "λ" is the wave length of the light in vacuum and n is the number of solute particles per cc. The molecular weight M is introduced into this expression through n, namely by replacing n by its equivalent cN/M, c being the grams of solute per cc. and N the Avogadro number. Since $(\mu - \mu_0)/c$ is sensibly constant for most substances at the low solute concentrations now under consideration, it becomes possible to write that the turbidity divided by the concentration is a constant. This is represented by equation (6):

$$\frac{\tau}{c} = HM \qquad (6)$$

Note that the constancy is represented by the product of the molecular weight and a factor H defined according to (7):

$$H = \frac{32\pi^3}{3}\frac{\mu_0^2}{N\lambda^4}\left(\frac{\mu - \mu_0}{c}\right)^2 \qquad (7)$$

In finding the molecular weight of a given solute at given concentration in solution, the turbidity has to be determined. Since this is generally quite small for the solutions under consideration, *i. e.*, the decrease in intensity undergone by the incident beam on passing through the solution is usually difficult to measure, light scattering measurements at 90° are resorted to. "H" is determined from a knowledge of the wave length of the incident light and the solution concentration, and the measurement of refractive index difference between solution and solvent. This difference is very small, so differential refractometer technique must be used.

Higher Concentrations (*3, 4, 8*). At higher concentrations in a system of small isotropic particles the relationship (6) breaks down. The particles are no longer that far apart that they can be considered as independent scatterers. A given amount of destructive interference results and the turbidity tapers off from its linearity with the concentration. This is illustrated by the shape of the curve in Figure 3.

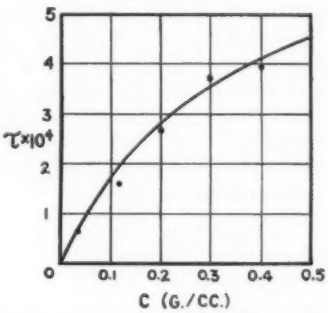

Figure 3. Turbidity versus Concentration of Aqueous Sucrose Solutions. Curve Calculated from Osmotic Pressure Data. Points Determined by 90° Scattering. Debye (*4*)

Actually, at sufficient proximity for small enough particles which are at fixed and regular distances from one another, *i. e.*, the crystal lattice, no light is scattered except parallel to the incident beam owing to the complete interference of the scattered wavelets. However, the particles under consideration are in Brownian movement and the randomness of their relative locations, present and future, is dictated thereby. The greater the degree of Brownian movement, the greater will be the degree of local inhomogeneities and there will be less interference of scattered rays.

This concept of local inhomogeneities was considered by Smoluchowski (*14, 15*) in explaining the great intensity of molecular scattering observed for liquids near their critical temperatures (critical opalescence). In a liquid, where the molecules are in continuous Brownian movement, it becomes conceivable that in a sufficiently small element of volume, the number of molecules in it, *i. e.*, the density of this element, will vary from instant to instant. In terms of the whole liquid, density fluctuations occur, these fluctuations being greater the more intense the Brownian activity. This, in general, is a maximum at the critical temperature where the light scattering is at its maximum. At the same time it is found that the isothermal compressibility coefficient β is proportional to the scattering, it also is increasing enormously in the vicinity of the critical point (Cabannes (*3*)).

Einstein's (*8*) work in this field pertained to the exact calculation of the amount of light scattered laterally by the opalescent material. For pure liquids:

$$\tau = \frac{8\pi^3}{3\lambda^4}(\epsilon_0 - 1)^2 kT\beta \qquad (8)$$

"ϵ_0" is the dielectric constant of the liquid and kT is the product of the Boltzmann constant and the absolute temperature.

Einstein applied the theory of thermodynamic fluctuations to solutions where now the fluctuating inhomogeneities in the solute, *i. e.*, concentration fluctuations, become important. These fluctuations avoid destructive interference of the scattered light which occurs especially when the particles are close together (higher concentrations). It is evident that the greater the concentration fluctuations (the more intense the Brownian movement) the less the interference and the greater the scattering. In writing an expression for the turbidity at higher concentrations, he paralleled the nonlinearity between τ and c with the nonlinearity between the osmotic pressure P (which depends on the Brownian movement intensity) and c also at higher concentrations. His general relation for the turbidity due to the solute in a suspension is:

$$\tau = \frac{32\pi^3}{3}\frac{\mu_0^2\,(c\partial\mu/\partial c)^2}{N\lambda^4 c\dfrac{\partial}{\partial c}\left(\dfrac{P}{RT}\right)} \qquad (9)$$

R being the gas constant.

Note that equation (9) reduces to equations (6) and (7) at the low concentrations where the relationships are linear. Namely, van't Hoff's ideal osmotic pressure law holds while τ is proportional to c, and the coefficient $\partial\mu/\partial c$ is sensibly constant so that it can be designated by $(\mu - \mu_0)/c$.

At the higher concentrations now under consideration, Debye, in making equation (9) workable, still treats the refractive index-concentration coefficient as constant. In order to resolve the coefficient $\dfrac{\partial}{\partial c}\left(\dfrac{P}{RT}\right)$ he employs the osmotic pressure formula:

$$\frac{P}{RT} = \frac{c}{M} + Bc^2 \qquad (10)$$

which is more representative of conditions at higher concentrations than the van't Hoff relation. "B" is a constant depending on the solvent.

Accordingly, equation (9) takes the form:

$$H\frac{c}{\tau} = \frac{1}{M} + 2Bc \qquad (11)$$

with H represented by equation (7). "τ" and H are evaluated as already described in the case of highly dilute systems.

Note the straight line relationship between c/τ and c. "M" can be evaluated from the intercept of the line with the c/τ axis. Figure 3 (*4*) is illustrative of the accuracy obtainable with equation (11). The points are actual turbidity measurements, and the curve has been calculated using osmotic pressure data. A molecular weight value of 380 was calculated for the sucrose from the turbidity measurements. This differs only by 10 per cent from the actual value which is 342.

SMALL ANISOTROPIC PARTICLES (*3, 4*)

As is often the case, the particles under consideration, although small, are anisotropic. Whereas the polarization induced in isotropic particles is independent of direction in the particle, the tendency in anisotropic particles is for the electric moments not to be of the same magnitude in all directions but to be influenced by the shape of the particle. As a result, the light scattered at 90° with the incident beam will have a certain percentage of the other component of polarization in it, resulting in a given amount of depolarization.

Since the total amount of scattering (at 90°) for an anisotropic particle is greater than that for an isotropic particle of the same molecular weight, corrections must be made in the turbidity light-scattering measurements obtained for the purpose of determining molecular weight. Debye (*4*) multiplies molecular weights (of anisotropic particles) by a factor based on Cabannes' (*3*) work. The relation given by Cabannes to show the additional scattering due to anisotropy is:

$$\frac{6(1+\rho)}{6-7\rho} \qquad (12)$$

"ρ" is the fraction of depolarization in the light scattered at 90° with the incident unpolarized beam. It (ρ) represents the ratio in the scattered light of the horizontal component of polarization (that component corresponding to the $\cos^2\theta$ term in the Rayleigh equation) divided by the vertical component (that component corresponding to the unity term).

The depolarization increases with the degree of anisotropy, and therefore it becomes possible to estimate the extent of deviation from isotropy by depolarization measurements. It is interesting to note in this connection that calculations show that the maximum depolarization which can be theoretically obtained from a particle small compared with the wave length of incident light, and which is an infinitely thin rod, is 50 per cent. Depolarization is 0 per cent for argon and 12.5 per cent for nitrous oxide. Aromatic compounds show greater depolarization than do corresponding aliphatics. Depolarization increases as one goes from ethane to ethylene to acetylene.

LARGER PARTICLES (*1, 2, 11, 12*)

When particles are greater than $^1/_{20}\lambda$ in at least one linear dimension, their light scattering no longer conforms to the relatively simple Rayleigh principle where the particle is regarded as a single dipole. The quantitative explanation is much more complicated since not only does each particle act as a multisource of scattered wavelets which tend to destructively interfere with each other, but also multipolar electric and magnetic fields become set up in the particle. As a result, the proportion of the incident beam scattered no longer varies as the sixth power of the radius (or major axis of the mole-

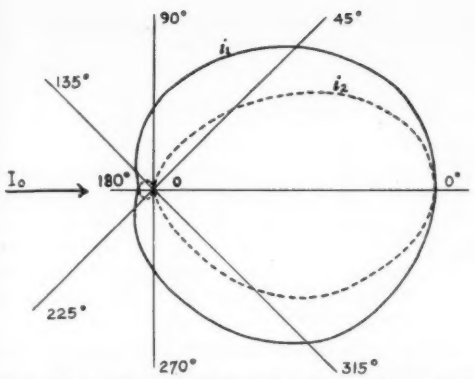

Figure 4. Relative Intensity of Scattering about Isotropic Particle of Radius almost 0.13λ. m = 1.25. Blumer (2)

cule), nor inversely as the fourth power of the wave length, these exponents decreasing in magnitude with larger particle size.

The scattering will now not have twofold symmetry, as illustrated in Figure 2, even if the large particle is spherical. Due to the difference in relative light paths, there will be more light scattered in the direction forward to the incident beam than backward because there are greater phase differences between the backward components and therefore the destructive interference is greater. Figure 4, which is based on calculations by Blumer (*2*), illustrates such difference in directional scattering occurring for a spherical particle of radius almost 0.13λ.

As in Figure 2, the particle is located at the origin 0 and the relative intensities of the scattered components i_1 and i_2 at a given angle (θ) with the incident beam are represented by the straight line distances between the origin and the continuous and dotted curves respectively, at the angle under consideration. The ratio of refractive index of particle to solvent is 1.25.

With increasing particle size, the light scattering diagram of a particle becomes much more complicated. Maxima and minima of scattering not only appear, but become more complex. Figure 5 illustrates maxima and minima for a spherical particle whose radius is almost 0.65λ. The large forward area of scattering is not shown.

These complexities in the pattern of intensities of scattered light about the particle increase as the refractive index of the particle relative to the solvent increases. Also, deviation of the particle shape from sphericity results in a more complicated pattern.

The maxima and minima of scattering by large particles show up at different angles (θ) depending on the incident wave length. Thus, when the incident light is white, given colors will be apparent at given angles and these bands will be more sharp the higher the degree of mono-dispersity of the suspension. This method of Tyndall spectra was used by La Mer and his co-workers (*1, 11, 12*) in investigating relatively iso-dispersed sulfur sols.

Mie Calculations—Spheres (*13*). It is only for spheres that formulas have been developed, which, by considering the multipolar electrical and magnetic effects occurring in the larger particles on exposure to light, relate the amount of light scattered to particle size, wave length of the incident light, and refractive index.

These formulas are due to Mie and consist of series expressions in which the coefficients are functions of the ratio (m) of the index of refraction of the particle and of the solvent, and the parameter (α) based on the particle radius (r) and the wave length of the incident light in the solvent medium (λ'), *i. e.*, $\alpha = 2\pi r/\lambda'$. The series are the sum of the contributions to the scattering by the electric and magnetic multipoles of the oscillating electrical charges in the particle. When the spheres are large and their refractive index relative to the solvent is appreciable, the calculations become very difficult.

For spherical particles having an index of refraction no greater than 1.33 times that of the solvent and a size not larger than $^1/_6$ of the wave length of the incident light, only the contributions to scattering by the electric dipole moment (a_1), the electric quadripole moment (a_2), and the magnetic dipole moment (p_1) are appreciable, and the scattering can be represented sufficiently accurately by equations (13):

$$\frac{i_1}{I_0} = \frac{\lambda'^2 n}{8\pi^2 d^2}\left[\frac{a_1}{2} + \frac{(a_2 + p_1)}{2}\cos\theta\right]^2$$

$$\frac{i_2}{I_0} = \frac{\lambda'^2 n}{8\pi^2 d^2}\left[\frac{a_1}{2}\cos\theta + \frac{a_2}{2}\cos 2\theta + p_1\right]^2 \qquad (13)$$

where

$$a_1 = 2\alpha^3\frac{(m^2 - 1)}{(m^2 + 2)} \qquad a_2 = \frac{-\alpha^5\,(m^2 - 1)}{6\,(m^2 + {}^2/_2)}$$

and

$$p_1 \simeq \frac{-\alpha^5}{15}(m^2 - 1)$$

"i_1" and i_2 are the intensities per cc. of the polarized

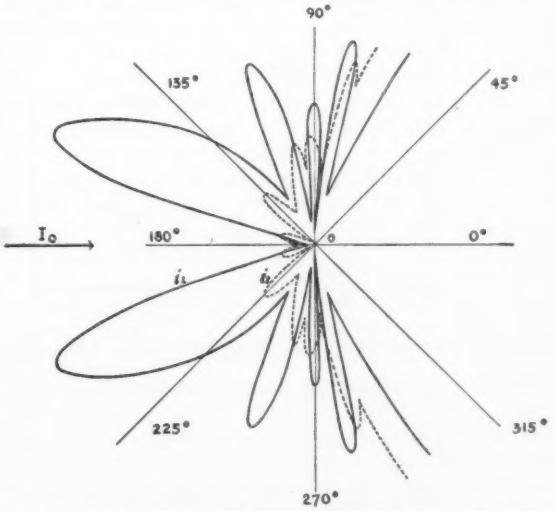

Figure 5. Relative Intensity of Scattering about Isotropic Particle of Radius almost 0.65λ. m = 1.25. Blumer (2)

components of the scattered light as already mentioned in connection with the Rayleigh equation, the incident light (I_0) being unpolarized. "n" represents the number of particles per cc. and d is the distance between the observer and the scattering system.

Note that as the particle becomes smaller, the electric quadripole and magnetic dipole moment values (a_2 and p_1 respectively) dwindle proportionately faster than the electric dipole (a_1) and eventually become negligible, with the result that equations (13) reduce to the Rayleigh equation (3).

Debye Approximate Treatment (4, 6, 13, 16). By working with systems in which the difference in optical constants between the particle and the surrounding medium is low, the problem of scattering by large particles may be simplified, for, according to Debye, under this modification, the distortion effect of the electric and magnetic fields in the particle on the primary (incident) light and the secondary (scattered) wavelets becomes minimized. As a result Debye finds it only necessary to allow for the interference between the scattered wavelets from a particle in deriving mathematical expressions which relate amount and direction of scattered light with size and shape characteristics of the molecules. This is quite an advance over the Mie formulations because not only can one satisfactorily treat spheres, but also other geometrically shaped molecules, such as rods and coils, may be covered as well.

The solute molecule is looked upon as divided into a series of independent dipole oscillators (submolecules) which radiate according to the Rayleigh principle. Then the average sum of the contributions of these submolecules is calculated in much the same manner as that followed for representing the interference effects observed with X-rays or electrons scattered by crystals, liquids, or gases.

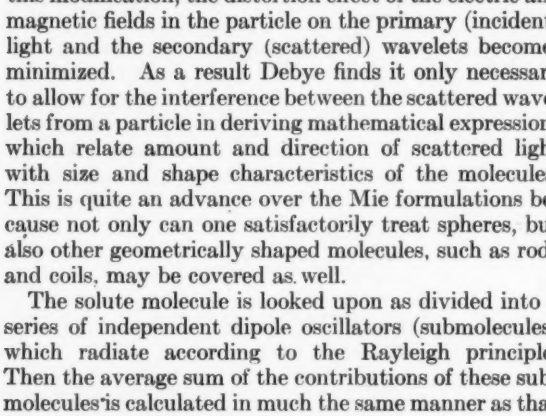

Figure 6. Dissymmetry ($I_{45°}/I_{135°}$) versus Particle Size. Oster (13)

Different equations are obtained depending on the configuration of the particle. Those equations developed for spherical, rodlike, and randomly coiled molecules are represented by equations (14), (15), and (16) below. Actually, the Mie theory (spherical particles) reduces to equation (14) when the particles are relatively small in size and the difference in index of refraction between particles and suspending medium is small.

Spheres

$$i_n = \left[\frac{3}{z^3}(\sin z - z\cos z)\right]^2 \qquad (14)$$

Coils

$$i_n = \frac{2}{t^2}\left[e^{-t} - (1 - t)\right] \qquad (15)$$

Rods

$$i_{n\theta} = \frac{1}{z}\int_0^{2z}\frac{\sin w}{w}dw - \left(\frac{\sin z}{z}\right)^2 \qquad (16)$$

"$i_{n\theta}$" is the normalized intensity of scattering at the angle θ with the proceeding incident beam. That is, it equals the quotient of the intensity of scattering at θ and at zero degrees. The z and t terms are functions of particle size L (which is the diameter in the case of spheres, the mean square distance between ends for coils, and length in the case of rods), wave length λ' of the incident light in the solvent, and the angle θ to the incident beam at which the scattered light intensity is considered:

$$z = \frac{2\pi L}{\lambda'}\sin\frac{\theta}{2}$$

$$t = \frac{8}{3}\left(\frac{\pi L}{\lambda'}\sin\frac{\theta}{2}\right)^2$$

"w" is the variable in the integral part of equation (16), when integration is carried out between the limits 0 and $2z$.

These equations bear out that as L increases, or λ' decreases, the ratio of scattering in the forward direction to that in the backward direction, *i. e.*, the dissymmetry, increases. Figure 6 illustrates this, the ratio $i_{n\,45°}/i_{n\,135°}$ being plotted against L divided by λ' for each of the three molecular configurations under discussion. Note how much more rapidly the dissymmetry increases with particle size for spheres versus coils and coils versus rods.

Figure 7 shows the complete angular distribution from $\theta = 45°$ to $\theta = 135°$ at a given wave length for tobacco mosaic virus particles. Their shapes are rodlike according to the electron microscope and their lengths have been estimated, with the aid of a plot like Figure 6, to be 103 $m\mu$ in the case of A and 275 $m\mu$ in the case of B. The straight line distance from the origin 0 to the curve at an angle with I_0 represents the normalized light scattering intensity at that given angle of observation with the incident beam. Note the considerable increase in dissymmetry which occurs when the rods are almost tripled in length.

The Debye approximate equations are useful in the estimation of the length (L) of the major axis of a particle; or, they can be employed to gain information about the shape.

In the determination of L, the particle shape must be known in order to find whether equation (14) or (15) or (16) is applicable. The intensity of light scattering for a given wave length at two different angles is meas-

ured, the measurements preferably being on either side of the normal with the incident beam and making the same angle with the normal. On substituting these values in the appropriate equation a value for L is obtained. This would be the diameter in the case of spheres, from which the molecular weight can be calculated provided the density of the solute is known.

With coils and rods, another property has to be known in order to determine the other shape dimensions of the molecule. This is the molecular weight, which could be determined by viscosity, osmotic pressure, sedimentation, etc. If the turbidity technique (light scattering at 90°) is employed, two kinds of corrections must be made on the actual measurement before it can be converted to a molecular weight value by equations (6) and (11). First, there is the factor which makes allowance for the depolarization due to the anisotropy of the particles (see page 18). Secondly, the light scattering interference effects have to be allowed for. This latter correction factor, which is the ratio of the intensity of scattering at 90° in the absence of intramolecular interference to the observed intensity, is greater the greater the dissymmetry, thus increasing with L. Particle shape may be obtained, in many cases, from electron microscope observations. Also, interpretation of results on centrifugal sedimentation, on viscosity, or on streaming birefringence, will yield useful information pertaining to the molecular geometry.

When using the Debye approximate equations for gaining information about particle shape, the dissymmetry, *i. e.*, $i_{\pi\ 45°}/i_{\pi\ 135°}$, is measured and substituted in equations (14), (15), and (16) respectively to obtain values of L in each case. Then the molecular weight is determined by any of the means, whichever is convenient, already mentioned. It is obvious that the particles are spheres if the value of L obtained from equation (14) corresponds to the diameter of a sphere of the given molecular weight, the density being known. Rods can be distinguished from coils when the width (of the particle chain) is known. Figure 6, which shows that for a given L/λ', the dissymmetry is greatest for spheres and least for rods, is helpful in this sort of a problem.

Use could be made of the fact that the dissymmetry curves in Figure 6 each approach distinct and different limiting values as L/λ' increases. By decreasing the wave length of the incident light so that L/λ' increases and making dissymmetry measurements, the shape and limiting tendency of the curve "dissymmetry versus L/λ'" can be evaluated and information pertaining to the molecular geometry can be obtained.

Stein and Doty (*16*) made dissymmetry measurements on cellulose acetate in acetone, and the results indicated that the molecules are just about fully extended at molecular weights below 80,000, but become less stretched-out as the size increases, the polymeric chain evidently beginning to coil back on itself. Their method was to measure the dissymmetry of different samples of different but known molecular weight (deter-

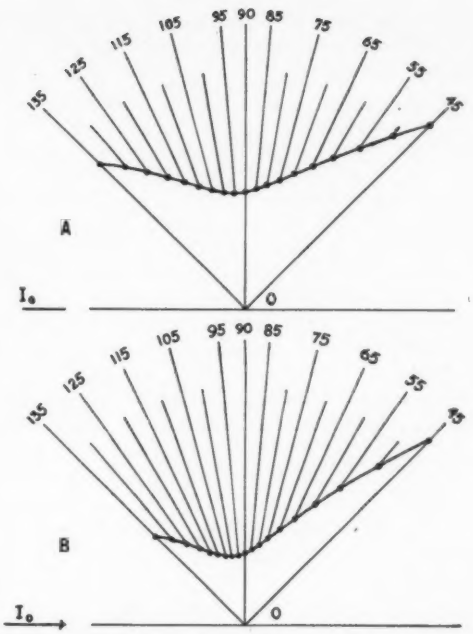

Figure 7. Angular Scattering for Rod-like Virus Particles at λ = 546 mμ. Length = 103 mμ in A and 275 mμ in B. Oster (*13*)

mined by osmotic pressure, viscosity, and turbidity-light-scattering techniques). With the aid of plots of dissymmetry versus L from equations (15) for coils and (16) for rods (see Figure 6), they estimated values for L for the molecules in the solutions if coils or rods and tabulated them alongside the lengths in each solution, calculated on the assumption that the molecules are completely extended, the monomer unit of the chain being 5.1 Å. as determined from X-ray studies.

Lately, dissymmetry studies have been used to advantage by Debye and Anacker (*5*, *6*) to show that cationic soap micelles have a rodlike structure. On the basis of energy considerations they allowed that the cationic molecules form aggregates with the hydrocarbon chains inward and the polar or ionic portions outward toward the suspending medium, and that the configuration of the aggregate could be a sphere where all the hydrocarbon tails meet at more or less of a common center; or a disc sandwich two molecule lengths thick where the hydrocarbon tail ends meet in the same central plane; or a rod of circular cross section (two molecule lengths diameter) where the polar parts of the molecules are at the surface of the rod and the hydrocarbon tail ends make up the interior, they lying perpendicular to the rod or cylinder axis. Then dissymmetry measurements were made and used in the different approximate equations to obtain corresponding values of L. With the aid of these values of L and the known length of the soap molecule, a molecular weight was calculated for each of the proposed micelle configurations. On comparison of these calculated molecular weights with the actual micelle molecular weight as found by turbidity measurements, it was

seen that that value obtained for the rods was in agreement, the disc and sphere calculated weights being very large in comparison.

DEPOLARIZATION (*9, 10, 13*)

Additional information pertaining to size range and shape of particles can be obtained by the analysis of the degree of depolarization existing in the light scattered, say at 90°. It will be recalled (page 16) that the light scattered at 90° by small particles is completely polarized if they are isotropic. If anisotropic, depolarization will be apparent, the relative amount of depolarization increasing as the particles become less isotropic.

However, isotropic or spherical particles also show depolarization when they are sufficiently large (see Figure 5 and equation (13)), this effect increasing with increasing particle radius. When the large particles are not spherical, there is still further depolarization due to the anisotropy. These characteristics, in addition to the circumstance that for a given system, the nature of the light scattered at 90° is different depending on whether the incident light is unpolarized, polarized in one direction, or polarized in the other direction, make it possible to classify scattering particles. The groups, small isotropic, large isotropic, small anisotropic, or large anisotropic thus could be distinguished according to the following (see Oster (*13*)):

(*a*) Small isotropic particles scatter light only if the incident light is unpolarized or if it is polarized in that direction corresponding to the unity term of $(1 + \cos^2 \theta)$ in the Rayleigh expression, that is, in the vertical direction. In either case, the scattered light is polarized, but only vertically. Scattering is zero if the incident light is polarized in the other direction.

(*b*) As the isotropic particles become larger, they also begin to scatter that component of polarization corresponding to the $\cos^2\theta$ term in the Rayleigh expression, when illuminated by that same component or by unpolarized light. The result is that for unpolarized incident light on large spheres there is a given amount of depolarization in the scattered light at 90°, this depolarization increasing with particle size. There is no depolarization if the particles are illuminated by incident light polarized in either strictly vertical or strictly horizontal direction.

(*c*) The main distinguishing feature between isotropic and nonisotropic particles is that, with anisotropy, depolarization exists in the scattered light even if the incident light is polarized. When the particles are small, the depolarization in the light they scatter at 90° is between 0 and 100 per cent if the incident light is polarized corresponding to the Rayleigh unity term, or if it is unpolarized. Depolarization is 100 per cent if the incident light is polarized in the other direction.

(*d*) When large anisotropic particles are being examined the properties of the scattered light represent a superposition of that for small anisotropic particles and large spheres. Thus, when the incident light is unpolarized, the depolarization in the scattered light is greater for large anisotropic particles than for large spheres. When the illumination is polarized according to the Rayleigh equation unity term the depolarization in the scattered light increases with particle size. However, when the illumination is polarized in the other direction the depolarization no longer remains at 100 per cent for larger (anisotropic) particles.

Depolarization measurements have been useful in showing changes in anisotropy of molecules with increasing size. For instance, it has been noted that molecules exhibit less anisotropy as they increase in weight (or chain length) thereby furnishing evidence that there is greater tendency to form more random coils.

SUMMARY

Quantitative information concerning size and shape of dispersed particles is obtainable by proper interpretation of the intensity and polarization of the light scattered from the solution at given angles with the incident light.

(1) When the particles are isotropic and small, *i. e.*, at least $^1/_{20}\ \lambda$, and the system highly dilute, the molecular weight may be evaluated by means of the Rayleigh concept (equation (3)), or the Debye treatment involving the turbidity as represented by equations (6) and (7).

(2) To determine the molecular weight of these small isotropic particles at higher concentrations use the general Debye treatment involving the turbidity. This is represented by equation (11).

(3) When the particles are anisotropic but still small, use the Cabannes factor (relation (12)) involving depolarization to correct the molecular weight obtained by the methods mentioned for the small isotropic particles.

(4) For isotropic (spherical) particles greater than $^1/_{20}\ \lambda$, the size can be determined with the aid of the Mie calculations.

(5) Or, the Debye approximate treatment (equation (14)) can be used to estimate the size of these larger spheres provided the difference in optical constants between the particle and surrounding medium is low. Similar treatment can be employed for coils (equation (15)) and rods (equation (16)). By comparison of data calculated with equations (14), (15), and (16), respectively, it becomes possible to classify the particle according to shape.

(6) Additional information concerning shape and size of particles may be available from considerations of the degree of depolarization in the scattered light.

TABLE OF NOMENCLATURE

a_1 = Contribution to light scattering by the electric dipole moment in the Mie equations.
a_2 = Contribution to light scattering by the electric quadripole moment in the Mie equations.
B = Constant in osmotic pressure formula.
c = Weight in grams of solute per cc.
d = Distance between the observer and the scattering system.
H = The proportionality constant between τ/c and M for small isotropic particles in a highly dilute system.

I = Amount of incident light.
I_0 = Initial amount of incident light which may be polarized or not as specified.
i_1, i_2 = Intensity of the polarized components of the scattered light.
$i_{s\theta}$ = Normalized scattered light intensity at the angle θ.
i_θ = Total light scattered at the angle θ with the incident beam.
k = Boltzmann constant.
L = Size factor in molecules, *i. e.*, diameter of sphere, mean square distance between ends of coil, or length of rod.
M = Molecular weight.
m = Ratio of the refractive index of the solute particles to that of the solvent itself.
N = Avogadro's number, *i. e.*, 6.02×10^{23}.
n = Number of particles per cc.
P = Osmotic pressure.
p_1 = Contribution to light scattering by the magnetic dipole moment in the Mie equations.
R = Gas constant.
r = Particle radius.
s = Density of the solute in grams per cc.
T = Absolute temperature.
$t = \frac{8}{3}\left[\frac{\pi L}{\lambda'} \sin \frac{\theta}{2}\right]^2$ = a term in the Debye approximate equations.
V = Volume of a light scattering particle.
w = Variable in definite integral which is part of the Debye approximate equation for rods.
x = Distance along the incident beam in the scattering solution.
$z = 2\pi L \sin(\theta/2)/\lambda'$ = a term in the Debye approximate equations.
$\alpha = 2\pi r/\lambda'$, term in the Mie equations.
β = Isothermal compressibility coefficient in volume decrease per unit initial volume per unit pressure difference.
ϵ_0 = Dielectric constant of the solvent.
θ = Angle with the line of the incident beam (proceeding from the particle or solution) at which scattered light from the particle(s) is being viewed.
λ = Wave length of the incident light in a vacuum.
λ' = Wave length of the incident light in the solvent in which the solute is contained.
μ = Index of refraction of the solution.
μ_0 = Index of refraction of the pure solvent.
ρ = Fraction of depolarization.
τ = The turbidity or the extinction due to scattering.

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THERMAL DIFFUSION COLUMNS FOR LECTURE DEMONSTRATION[1]

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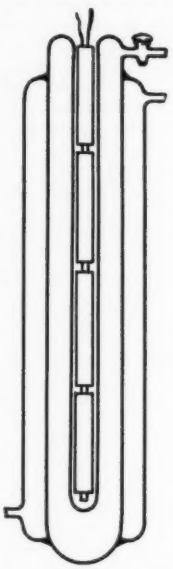
A DEMONSTRATION of thermal diffusion which can be performed during a lecture period has not been described in the literature. It is the purpose of this article to describe the design of thermal diffusion columns suitable for this purpose.



Suitable thermal diffusion columns should have the following characteristics:

(1) Short equilibrium time so that the separation can be observed during the lecture. The shorter the equilibrium time the more effective will be the demonstration. Also, the column should not be too large.

(2) Readily observed separation. The separation should be large and should be easily visible. Bromine and helium are the best pair of gases, or bromine and air can be used if helium is not available. A mixture of a radioactive and nonradioactive gas could be used if desired and the separation followed with counters at each end of the column.

DESIGN OF COLUMN

The theory of the thermal diffusion column has been discussed in detail by Jones and Furry,[3] and the design of columns which have a minimum of either length, volume, or equilibrium time for a given separation has been discussed by Whalley.[4]

The separation is described in terms of a factor F defined by

$$F = \frac{\log q_c}{\log q_n} \text{ or } q_c = q_n^F \qquad (1)$$

where q_c is the separation factor (ratio of the concentration ratios in mol fractions at each end) of the thermal diffusion column and q_n is the separation factor of a nonconvective unit with the same hot and cold temperatures. If the separation is small it is easily shown that

$$\Delta C_c = F \Delta C_n \qquad (2)$$

where ΔC_c and ΔC_n are the concentration differences of one molecular species obtained in the convective and nonconvective apparatus respectively. F is given in equations (33–6) of ref. (2) in terms of the properties of the gas and the dimensions of the apparatus.

The lengths L, wall separations d, and relaxation times t for thermal diffusion columns without reservoirs corresponding to minimum length, volume, or relaxation time are given by the equations:

$$L = \beta_L F_f (AP^2)^{-1/3} \qquad (3)$$

$$d = (\beta_d R P^4)^{-1/5} \qquad (4)$$

$$t = \beta_t M P L^2 \qquad (5)$$

where the β's are simple numbers dependent on the quantity to be minimized. The values of the β's are given in Table 1.

TABLE 1

Minimum	β_L	β_d	β_t
Length	2.129	2	$^2/_3$
Volume	2.311	5	0.9804
Relaxation time	2.682	$^1/_2$	$^1/_3$

The remaining quantities in equations (3–5) are:

$$A = \frac{\rho g}{720 \eta D} \frac{\Delta T}{\overline{T}}$$

$$R = \frac{10}{7} A^2 \frac{f_c}{f_d}$$

$$M = (\pi^2 D)^{-1}$$

$$f_1 = \frac{f_d}{f_h} \left(\frac{f_c}{f_d} \right)^{1/3}$$

where ρ is the density, η the viscosity, D the diffusion coefficient of the gas mixture at 1 atm., P the pressure in atmospheres, g the acceleration due to gravity, and f_c, f_d, and f_h are correction factors for the cylindricity of the column and are given in ref. (1), equations (100–11). $\Delta T = T_2 - T_1$, and $\overline{T} = {}^1/_2(T_2 + T_1)$, where T_1 and T_2 are the cold and hot wall temperatures. The value of d it will be noted is independent of the separation required.

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[1]. Issued by the National Research Laboratories as N. R. C. No. 2590.

[2]. National Research Laboratories Post-Doctoral Fellow.

Note added in proof. Since this paper was written our attention has been drawn to a paper by B. B. McINTEER and C. E. SCHENSTEDT (*Am. J. Phys.*, **17**, 417 (1949), describing a hot wire column using helium and air. The separation is observed by the color of the hot wire and equilibrium is reached in about 20 min. However the column is neither so easy to make and operate nor so rapid as ours.

[3] JONES, R. C., AND W. H. FURRY, *Rev. Mod. Phys.*, **18**, 151 (1946).

[4] Whalley, E., *Trans. Faraday Soc.*, **47**, 129 (1951).

EXPERIMENTAL

The columns are filled with an equimolecular mixture of bromine and helium and bromine and air respectively at a total pressure of 150 mm. of mercury (0.197 atm.). This pressure is low enough to prevent the bromine from condensing when it is concentrated at the lower end of the columns. They are made of standard pyrex tubing, as shown in the figure, with the dimensions given in

TABLE 2
Dimensions of Columns

	Br_2-He	*Br_2-air*
Outer diam. of inner tube	12 mm.	15 mm.
Inner diam. of outer tube	34 mm.	31 mm.
Length	40 cm.	70 cm.

Table 2. The dimensions are not the optimum ones, but the nearest which could be obtained with standard glass tubing. The dimensions are not very critical and can be varied by 10–15 per cent without seriously affecting the efficiency of the column. The heaters for the inner tube are loops of B & S No. 11 chromel-A wire threaded through twin-bore porcelain insulators and controlled by a Variac transformer. The outer tube is cooled by a water jacket. The rate of heating of the inner tube is important in determining the rate of separation, and a high initial input which can be reduced later increases the rate. With an initial input of about 800 watts there is a noticeable separation in about 60 seconds with the helium-bromine column and in about 80 seconds with the air-bromine column. The top of the column is clear in about two minutes and four minutes respectively. Comparison between the theoretical and calculated equilibrium times is not attempted because the inner tube is heating up for a considerable part of the time required to clear the top of the column, and also no measurements are made of the temperature of the hot wall.

ODD HASSEL

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ODD HASSEL, the eminent Norwegian physical chemist, was born at Oslo on May 17, 1897. After graduation from the University of Oslo in 1920, he continued (1922–25) his studies at Munich and then at Berlin. He held a Rockefeller Fellowship, 1924–25. The Ph.D. was conferred by the University of Berlin in 1924. From 1925 to 1934 Dr. Hassel was lecturer in physical chemistry at Oslo; in 1934 he was advanced to a full professorship, a position he has completely held up to the present day.

His researches have dealt mostly with various topics in physical chemistry. A steady stream of worth-while papers have come from his laboratory. His chief interests have centered around crystal structure and molecular structure. His conclusions have been based on X-ray diffraction studies, measurements of dipole moments, and investigation of scattering of electrons by vapors. Since 1939 the "rotating sector" method of electron diffraction has been developed in his laboratory and applied to a series of problems relating to the establishment of the configuration of "free" molecules. Papers dealing with the significance of van der Waals distances in separate molecules, especially with reference to cyclohexane and its derivatives, decalin, and other six-membered rings, have been worthy of special notice. He has made an extensive study of the structure of *cis* decalin and a series of cyclohexane derivatives (including benzene hexachloride). In the field of preparative chemistry he has explored the preparation of the cylohexane series and related compounds.

Professor Hassel's "Kristallchemie" was published at Dresden in 1934; following an urgent demand, an English translation by R. C. Evans, "Crystal Chemistry," was issued the next year.

A member of the Norwegian Academy of Science since 1933, Professor Hassel also belongs to the Norwegian Research Council for Science and Humanities, and since 1949 has been chairman of its Mathematics and Natural Science section. He has been Norwegian Editor of *Acta Chimica Scandinavica* since 1947.

Professor Hassel received the Fridtjof Nansen Award in 1946; in 1950 the University of Copenhagen conferred the Ph.D. *honoris causa* on this distinguished Scandinavian chemist.

JOHN FREDERIC DANIELL

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JOHN FREDERIC DANIELL, inventor of the Daniell cell, is not considered a pioneer in the organization of a branch of chemistry or a school of thought, neither were his contributions to the field of science as voluminous nor as outstanding as those of his contemporaries which include Faraday, Dumas, Avogadro, Berzelius, and Graham. His services, however, to more than one branch of science, were of the quality to merit not only the highest honor of the Royal Society, but every medal given by the Society.

Only one account of the life of Daniell has been published. This is the obituary appearing in *Philosophical Magazine*.[1] Most of the references to Daniell's life are taken from this presentation made by the president of the Society, The Marquis of Northampton.[2]

John Frederic Daniell was born March 12, 1790, in a small town in England called Strand. His father, George Daniell, a Bencher of the Inner Temple, provided him with a good classical education in his own home. His father had visions of his son becoming a minister, but showed no signs of disappointment when he exhibited an early fondness for scientific pursuits. As a young man he was given a position in the sugar refining establishment of a relative where he introduced important improvements in its manufacture. However, the rigors of business were of little interest to him and he soon surrendered his position.

When he was 23 years old he was elected a Fellow of the Royal Society in whose activities he actively participated until his death.

In 1814–15 Daniell began work on solutions and crystals in which he discovered and exhibited the advantages of the utilization of water and different solvents over mechanical division of crystals in determining crystalline structures.[3] He noticed that if "amorphous alum" was left for some weeks in water it assumed a pyramidal form, and the lower part of it was embossed by distinct octahedral crystals. Borax exhibits similar properties giving rhomboidal crystals. Daniell concluded that ". . . in these cases the cohesion of the solid resisted unequally the solvent power of the liquid. . . ."

Similar work followed in which he attempted the investigation of the structures of various metals and salts by observing the formation of embossments upon dissolving the sample in suitable solvents.[4] He concluded that salts of some metals, including bismuth, antimony, and nickel, exhibited crystalline type structures. In 1818 he published his first theoretical explanation of the density of crystals through a consideration of spherical atoms and their relation to structure and density.[5]

In 1820, by the invention of the hygrometer, which bears his name, Daniell first gave precision to the means of determining the moisture of the atmosphere.[6] Early in life he became interested in meteorological phenomena. This interest resulted in the publication of 13 papers and one book on meteorology in addition to 27 original contributions in other fields, primarily subjects of a chemical and physical nature. In 1823 he published his "Meteorological Essays." This was the first attempt to collect the scattered facts on this particular subject, and to explain the most important phenomena of the atmosphere by means of physical laws. His model record of atmospheric changes is indicative of his emphasis on extreme accuracy in scientific observations. He organized the plan adopted by the Horticultural Society for their annual Meteorological Reports which became the model from which the Greenwich Meteorological Reports were developed.

Even though his pursuits shifted to other fields, his interest in meteorology continued. In 1839 he drew up the meteorological portion of the directions for the scientific observations to be made by government officers throughout the British Empire. In 1824, in an essay to the Horticultural Society, he called attention to the necessity of attending to the moisture of hothouses which caused a revolution in the construction of such establishments.[7] For this paper he received the Silver Medal of the Society.

In 1830 Daniell constructed a barometer for the Royal Society in which water was used as the fluid instead of mercury.[8] This required an instrument of enormous height, and only after mastering numerous problems of construction was his task completed. This barometer remained the most accurate in England for several years. He was engaged in its adjustment a few weeks before his death.

In the same year he devised a pyrometer for the measurement of high temperatures.[9] By the use of this instrument Daniell determined the melting point of iron to be about 3400°F.[10] From previous experi-

[1] *Phil. Mag.*, **28**, 409–12 (1846).
[2] The account was probably written by William Thomas Brande, Esq., Chairman of the Chemistry Committee of the Royal Society.
[3] THOMPSON, T., *Ann. Phil.*, **6**, 454–5 (1815).
[4] *Quart. J. Sci.*, **2**, 278–93 (1817).
[5] *Ibid.*, **4**, 30–42 (1818).
[6] *Ibid.*, **8**, 298–336 (1820).
[7] THOMPSON, T., *Ann. Phil.*, **27**, 114–30 (1826).
[8] *Phil. Trans.*, **122**, 539–74 (1832).
[9] *Ibid.*, **120**, 257–86 (1830).
[10] The present melting point of iron is considered to be 2793° F., from LANGE, N. A., "Handbook of Chemistry," 7th ed., Handbook Publishers, Inc., 1949.

ments by M. Guyton de Morveau, who used platinum expansion, Daniell calculated the melting point of iron to be 8696°F.[11] In his attack on the assumptions made by de Morveau he points out the impracticability of the old pyrometer. This tremendous improvement in the accuracy of determining high temperatures won him the Rumford Medal.

When King's College, London, was founded in 1831, Daniell was appointed Professor of Chemistry, where his attentions were turned to the phenomena presented by voltaic electricity. His interest in this particular problem had its roots in the experiments of Faraday.[12]

In Daniell's first letter to Faraday on voltaic combinations he exhibits proof of the source of his interest.[13]

> You know how deep an interest I have taken in your "Experimental Researches in Electricity," and how zealously I have availed myself of the opportunities, which you have ever kindly afforded me, of profiting by your oral explanation of such difficulties as occurred to me in the study of your last series of papers in the Philosophical Transactions.

It is in this publication that Daniell introduces an explanation of a constant voltaic combination which is still in use and has become a classical illustration of a battery. While repeating some of the experiments of Faraday, Daniell became conscious of the need for a voltaic combination which would furnish a constant force of sufficient magnitude to allow a prolonged investigation of the principles of electrolysis advanced by Faraday. He promptly discovered the cell which carries his name. In repeating Faraday's experiments using this new cell, which produced a constant current for days of continuous operation, Daniell happily reported that he observed no deviations from the results reported by Faraday. He published his findings in the same letter in which he described his cell.

An unfortunate incident made this simultaneous report possible. The notes of all experiments made by Daniell on the constant cell and subsequent experiments were lost. This necessitated his repeating all experiments of importance, the results of which were published in 1836, almost one year later than they should have been had this incident not occurred.

Five additional letters on voltaic combinations and subsequent applications supplemented the first, the last appearing in the *Philosophical Transactions* in 1842.[14] For this very important contribution to the scientific world, the Royal Society in 1836 awarded him their highest medal, the Copley Medal.

In 1839 Daniell's book, "Introduction to Chemical Philosophy," was published. This volume was perhaps the most original book on the subject published in this period.

For work on the electrolysis of salt solutions he was awarded the Royal Medal in 1842, the same year that he received the honorary degree of Doctor of Civil Law from Oxford. The first publication on this problem appeared in 1840.[15] He started from the fundamental principle that "the force which is measured by its definite action at any one point of a circuit cannot perform more than one equivalent proportion of work at any other point of the same circuit." Applying this principle to the results of the measurements he made of the quantities of hydrogen and oxygen liberated at the cathode and anode during the electrolysis of aqueous sulfuric acid, sodium sulfate, and potassium sulfate, and of the quantities of the same gases liberated by passing the same current, simultaneously, through acidulated water, Daniell concluded that the water was not decomposed in the changes, but only the acid or the salt was electrolyzed. He concluded that the salt was separated into two ions, "an anion composed of one equivalent of sulphur and four equivalents of oxygen, and the metallic cathion sodium." He gave the following electrolytic formulas to the salts he examined:

	Chemical formula	*Electrolytic formula*
Sulphate of Soda	$(S + 3O) + (Na + O)$	$(S + 4O) + Na$
Sulphate of Potassa	$(S + 3O) + (Ka + O)$	$(S + 4O) + Ka$
Nitrate of Potassa	$(N + 5O) + (Ka + O)$	$(N + 6O) + Ka$
Phosphate of Soda	$(P + 2^1/_2O) + (Na + O)$	$(P + 3^1/_2O) + Na$
Sulphate of Copper	$(S + 3O) + (Cu + O)$	$(S + 4O) + Cu$

By a similar experiment Daniell concluded that salts of ammonia were compounds of negative ions with the positive radical ammonium.

Measurements made by Daniell and Miller[16] showed that although the quantities of the anion and the cation liberated at the electrodes were always strictly equivalent, the number of cations which travel to the cathode in a given time is usually not so large as the number of anions which travel to the anode in the same time. They were searching for a means for studying in detail the quantitative ratio of transfer of ions to the electrodes. It is very likely that a procedure would have been worked out for a thorough study had not Daniell's sudden death ended this work. This problem was solved by Hittorf in the years 1853 to 1859.[17]

On March 13, 1845, Daniell attended a council meeting of the Royal Society, of which he was foreign secretary, and shortly after commenting on an item of business was apparently seized with apoplexy. The attentions of the physicians present were fruitless and in five minutes his life had ended, at 55 years of age. He was survived by two sons and five daughters. His wife had died in 1834, only two years before Daniell made his greatest contribution to the scientific world, the constant battery. William Allen Miller, his co-

[11] *Phil. Trans.*, **120**, 260 (1830).
[12] Faraday's laws of electrolysis were published in 1834.
[13] *Phil. Trans.*, **126**, 107 (1836).
[14] *Ibid.*, **130**, 137–56 (1842).
[15] *Phil. Mag.*, **17**, 349–56 (1840).
[16] *Phil. Trans.*, **134**, 1–19 (1844).
[17] "Ueber die Wanderungen der Ionen während der Elektrolyse," *Pogg. Ann.*, **89**, 177; **98**, 1; **103**, 1; **106**, 336, 513 (1853 to 1859). Cited by MUIR, M. PATTISON, "History of Chemical Theories and Laws," John Wiley & Sons, Inc., New York, **1907**.

worker on the electrolysis of salts, succeeded him as Professor of Chemistry at King's College.

His "Meterological Essays" appeared in a third edition the year of his death; his "Introduction to Chemical Philosophy" in a second edition in 1843. Both books were authoritative publications in their respective fields for several years after the author's death.

His success as a teacher is, without a doubt, due, in part, to his character and personality. The writer of his obituary states it thus:

> High as were his scientific attainments, he possessed others of a still lofty and more enduring character; to the sterling qualities of a vigorous understanding, and a kind and benevolent heart, he united the humble and unobtrusive piety of a sincere Christian.[18]

ACKNOWLEDGMENT

The author, a graduate student, wishes to thank Dr. Clara deMilt for suggesting the topic of this paper and for correcting the manuscript.

[18] *Phil. Mag.*, **28**, 412 (1846).

A NEW TYPE OF TRANSPARENT PROJECTION SLIDE

JON H. MYER
University of Southern California, Los Angeles, California

WHILE preparing projection slides for use in our chemistry classes,[1] a method of slide preparation was sought which would permit direct drawing or tracing onto a matte glass plate; yet would result in a completely transparent final slide. It is well known that pencil or India-ink tracings may be made directly on matte glass plates, but the resulting slide is not really suitable, since transmission of light through the matte plate is poor—resulting in a dull dark background even with powerful lantern illumination. By a simple procedure, however, it is possible to make the matte plate completely and brilliantly transparent. The principle employed for this and similar purposes utilizes the fact that a rough matte glass surface becomes completely transparent if covered with a clear oil, lacquer, or glue which has the same refractive index as the glass plate. To protect the slide surface and to avoid any lens effects it was found desirable to cover the treated plate with a second clear glass plate, just as is done in binding photographic plates. The method is given in detail below. It was also found convenient and quite economical to prepare ground-glass plates in our own laboratory, and the method of making these is also described briefly. Slides made by this process are completely transparent, permanent, protected from scratches and dust, very sturdy, and inexpensive to prepare.

Procedure for Preparing the Slides. The text, formula, or drawing to be projected is drawn on a matte glass plate, using India ink and a fine nib, or a drawing pencil of medium hardness. A little practice in the use of India ink on the matte glass surface may be required, but excellent results can easily be obtained. Errors may be easily corrected with a hard eraser, and if necessary the whole matte glass surface may be restored with a scouring powder.

After the slide has been drawn, and well dried if ink has been used, it is made transparent by applying Permount solution.[2] In the case of a $3^1/_4$- × 4-in. slide, 1 ml. of the thickened sirupy solution is applied to the center of the matte plate and a clear slide-plate is pressed on. Any air bubbles are driven to the edge by even application of pressure. This cement has the same refractive index as the glass of which the plates are made and proved superior to Canada balsam, vinyl acetate-chloride copolymer, etc.

Matte glass slides can be obtained commercially[3] or may be prepared as follows: A heavy glass plate is covered with a sheet of damp paper. On this non-slip flat base a standard projection slide is ground with the aid of another slide and 320-mesh Carborundum. The Carborundum is mixed with water and the two plates are ground together with a circular motion using even pressure. With some practice two slides can be made in this way within two to three minutes. After rinsing and drying, the plates are ready for use. Considerable experimentation showed that the 320-mesh Carborundum gave optimum results.

The completed slide-sandwich is dried for 24 hours at 37°C., and bound in the usual manner.[4]

[1] KHARASCH, N., "The use of lantern slides in the teaching of undergraduate chemistry," J. CHEM. EDUC., **28**, 280 (1951).

[2] This is a plastic cover-glass cement sold by Fisher Scientific Company, Catalogue No. So-P-15. It should be thickened by partial evaporation.

[3] Available from Keystone View Company.

[4] We found Mystik Tape ($^3/_4$ in. wide) convenient.

THE CHEMOTHERAPY OF TUBERCULOSIS[1]

H. HERBERT FOX
Hoffmann-La Roche, Inc., Nutley, New Jersey

FROM the standpoint of the chemotherapy of tuberculosis, these are stirring times, because there is at present a very widespread and intensive—if unpublicized—search being made for compounds useful in the treatment of tuberculosis. That this search will be fruitful can hardly be doubted, and it is not improbable that significant advances in this field will soon be forthcoming.

Before embarking upon a detailed discussion of the various substances which have so far shown some activity against tuberculosis, it is perhaps pertinent to consider briefly the character of the disease itself.

Historically—as is evidenced by archaeologic discoveries of skeletons with tuberculous lesions—tuberculosis has plagued mankind since remote antiquity and all through the subsequent ages has stood high on the list of man-killing diseases. Even today, in this era of modern sanitation, balanced diets, and vitamins, tuberculosis ranks seventh among the causes of death and is number one killer of persons between 15 and 45 years of age. Moreover, for each death it is estimated that there are five clinical cases. In 1941, for example, there were 60,000 deaths and approximately 300,000 clinical cases in the United States.

THE DISEASE

The disease is characterized by the formation in the tissues of nodular bodies or tubercles (hence, tuberculosis) and is manifested symptomatically in the pulmonary form by fever, cough, and progressive loss of weight (hence consumption). The causative agent, first isolated by Koch in 1882, is a fungus-like bacterium known as *Mycobacterium tuberculosis* or the tubercle bacillus. This organism has the unhappy ability of infecting practically any tissue or organ of the body, so that, in addition to the common pulmonary tuberculosis, there is tuberculosis laryngitis, enteritis, osteomyelitis, meningitis, and a host of others, including the rapidly fatal form known as miliary tuberculosis or "galloping consumption."

Tuberculosis is an infectious disease to which all humans are apparently susceptible. At any rate, there is conclusive evidence which shows that over 90 per cent of persons living in civilized communities have been infected before reaching adulthood. Fortunately, the vast majority of these infections are mild and are clinically asymptomatic. When, however, the disease becomes well established in a patient its treatment is usually a long drawn-out and very costly process. This resistance to treatment is at once one of the most outstanding and most deplorable characteristics of the disease. In this age of "wonder drugs," when almost all bacterial invasions are casually and quickly crushed with antibiotics or with the "sulfas," tuberculosis in its intractableness is almost unique. It is difficult to overemphasize this point. Despite streptomycin, tibione, *p*-aminosalicylic acid, and the other antituberculosis agents currently employed, there is no short and easy cure for the disease. In fact, strictly speaking there is no cure at all. The chemotherapeutic agents now in use do not kill and eradicate the tubercle bacillus. At best, they are tuberculostats and merely arrest the progress of the disease. This is, in truth, neither more nor less than what most of the so-called "wonder drugs" do in other bacterial diseases. The difference lies in the fact that the host-parasite relationship which exists in the common bacterial infections is unlike that which exists in tuberculosis. For example, in a staphylococcus or streptococcus infection, there is a relatively brief, all-or-none struggle between the host and the parasite and one or the other quickly succumbs. Today, thanks to chemotherapy, it is generally the parasite that loses. In tuberculosis, on the other hand, the organism can remain viable in the host for long periods without provoking an all-or-none struggle. Moreover, the host's defensive mechanisms are less certain and slower in action. Therefore, even though the tuberculostat has suppressed the disease, the host is not capable of effecting a rapid destruction of the tubercle bacillus. There are other factors which hinder the action of the chemotherapeutic agents. For example, in the caseous type of pulmonary tuberculosis, some of the organisms are frequently isolated within the cavity and cannot be reached by the drug. As an end result of these difficulties, the tuberculostats are currently employed in appropriately selected cases as valuable supplements to the traditional treatment of bed rest, collapse therapy, and surgery.

A detailed discussion of the various methods used to determine the antituberculosis activity of compounds is beyond the scope of this article. It is worth noting, however, that the *in vitro* tests which were first widely used in screening techniques are now largely in discard in some quarters, because it was quickly discovered that scores of compounds which showed high *in vitro* activity were completely inactive *in vivo*.

THE ANTIBIOTICS

The chemotherapeutic agents for tuberculosis may be divided into two main classes: the antibiotics and the synthetic tuberculostats. At present, the anti-

[1] Presented at the 13th Summer Conference of the New England Association of Chemistry Teachers, University of Rhode Island, Kingston, Rhode Island, August 23, 1951.

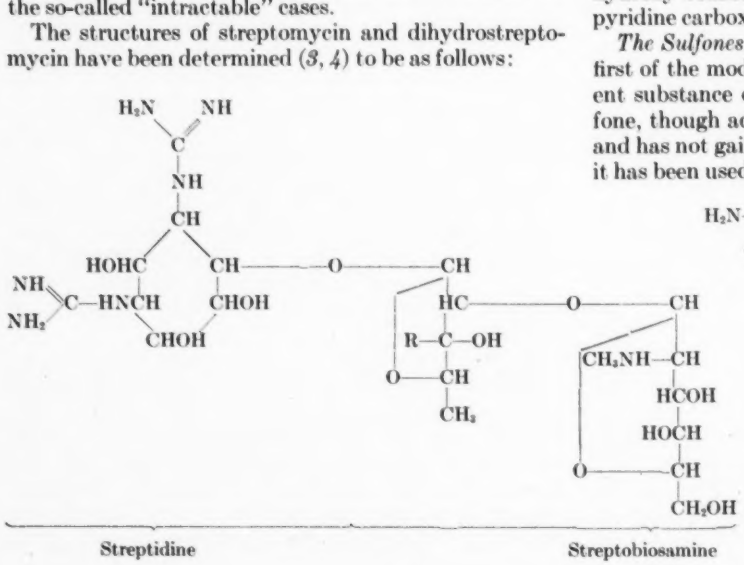
biotics are clinically the most important. This does not mean that many of them are active against tuberculosis—quite the contrary. Of the hundreds of antibiotics that have been isolated and screened during the last few years, only a handful have shown any promise and only two have been clinically approved.

Streptomycin, a metabolic product of *Streptomyces griseus*, was isolated in 1944 by Schatz, Bugie, and Waksman (*1*) and in the intervening years has shown itself to be the most effective agent available for the treatment of miliary tuberculosis, pulmomary tuberculosis, and tuberculous meningitis. It is not, however, an unmixed blessing. Severe side reactions are frequently encountered. These include chills, fever, nausea, vomiting, renal damage, blood dyscrasia, disturbances in vestibular functions with accompanying vertigo, and irreversible nerve deafness. Another and perhaps most serious disadvantage attending the use of streptomycin is the rapidity with which resistant strains develop. This effect has been partially mitigated by the concomitant administration of *p*-aminosalicylic acid.

Dihydrostreptomycin was developed in an effort to find a less toxic substitute for streptomycin (*2*). It is equally as active as the parent compound and possesses practically all of the disadvantages of the latter, though apparently to a somewhat lesser degree. Moreover, organisms resistant to one are resistant to the other.

In addition to the development of resistant strains, some cases which are apparently suitable for streptomycin or dihydrostreptomycin therapy fail to respond, for some obscure reason, to either drug. These are the so-called "intractable" cases.

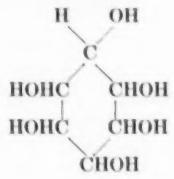
The structures of streptomycin and dihydrostreptomycin have been determined (*3*, *4*) to be as follows:



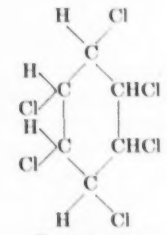
Streptidine — Streptobiosamine

Streptomycin: R = —C(=NH)—NH—C(=O)—H
Dihydrostreptomycin: R = —CH_2OH

It is interesting to note that the streptidine moiety is a diguanidino derivative of a constituent of heart muscle, inositol, and is also related to the new insecticide, lindane or gammexane.



Inositol



Gammexane

In addition to streptomycin, Waksman and his coworkers have discovered neomycin (*5*), a new antibiotic which has been found to be effective in extrapulmonary tuberculosis. It does not seem to be particularly good in the pulmonary forms and is apparently useless in tuberculous meningitis.

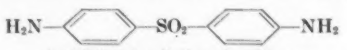
Viomycin, isolated independently by two different groups, has not yet been sufficiently studied to warrant a critical evaluation, but its activity is only about one-fourth that of streptomycin.

Mycomycin (*6*), discovered in 1946, has shown considerable *in vivo* activity, but it is too unstable to be practical.

SYNTHETIC TUBERCULOSTATS

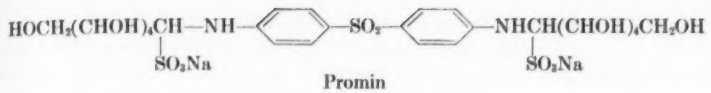
The synthetic tuberculostats may be divided into four principal categories: the sulfones, the amino hydroxy benzoic acids, the thiosemicarbazones, and the pyridine carboxylic acid derivatives.

The Sulfones. Chronologically, the sulfones are the first of the modern synthetic tuberculostats. The parent substance of this group, 4,4′-diaminodiphenyl sulfone, though actively tuberculostatic (*7*), is very toxic and has not gained clinical favor in tuberculosis, though it has been used with some success in leprosy (*8*).

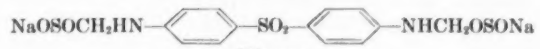


4,4′-Diaminodiphenyl sulfone

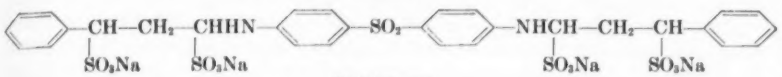
Many attempts have been made to increase the activity and solubility and decrease the toxicity of 4,4′-diaminodiphenyl sulfone. Compounds such as promin (*9*), diasone (*10*,*11*), and sulphetrone (*12*) are only partial successes, since, though the solubilities are increased and the toxicities are decreased, the activities are also somewhat decreased. It is strongly suspected that these latter compounds owe their activities to the fact that they are degraded in the body to the parent compound.



Promin

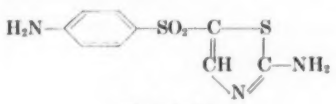


Diasone



Sulphetrone

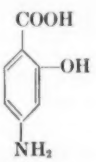
Substitution of a thiazole ring for one of the phenyl groups in 4, 4′-diaminodiphenyl sulfone results in promizole (*13*) which appears to be somewhat better than the other sulfones (*14*).



Promizole

None of the sulfones is sufficiently tuberculostatic to serve effectively as the sole chemotherapeutic agent in the treatment of clinical tuberculosis, but the better ones may find usefulness as adjuvants to streptomycin therapy.

Aminohydroxybenzoic Acids. The principal member of this group is *p*-aminosalicylic acid, commonly known as PAS. The discovery of the tuberculostatic activity of PAS was occasioned by Bernheim's (*15*, *16*) observation that the oxygen uptake of the tubercle bacillus increased under the influence of benzoates and salicylates. Lehmann (*17*), of Sweden, investigating this phenomenon with a large number of related compounds, found that *p*-aminosalicylic acid was markedly tuberculostatic.



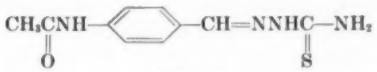
PAS

Though, as compared to streptomycin, the activity of PAS is low, it has been used extensively in clinical tuberculosis because it is atoxic. Unfortunately, its absorption and excretion are so rapid that to maintain adequate blood levels it must be given in large and frequent doses. Many variations in structure have been investigated, but none of them is superior to PAS itself. It is known that the hydroxy group in position 2 is necessary, since changing it to an amino or chloro group abolishes activity and shifting its position diminishes the activity. The amino group in position 4 also cannot be changed or shifted without decreasing activity. Similarly, esterification of the carboxy group or alkylation of the amino group reduces the activity markedly.

The pyridine analogue of PAS, 3-hydroxyisonicotinic acid, has been prepared by the author and has been found devoid of activity.

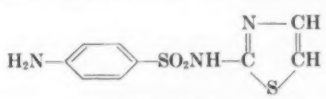
Although of limited usefulness alone, PAS is being ever more widely used as an adjuvant to streptomycin therapy, since a considerable body of evidence has been compiled to show that the conjoint use of both drugs retards the appearance of resistant strains.

The Thiosemicarbazones. The most active synthetic tuberculostats known belong to the thiosemicarbazones, and of these, the best known is tibione (also known as conteben, amithiozone, myvisone, or *p*-acetamidobenzaldehyde thiosemicarbazone) (*18*), *19*).

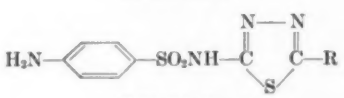


Tibione

The investigations into the field of thiosemicarbazones started originally with Domagk's observation that of the many sulfa drugs known, two (sulfathiazole and sulfathiadiazole) showed a limited *in vivo* tuberculostatic activity. In an attempt to establish

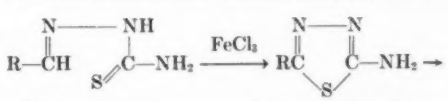


Sulfathiazole

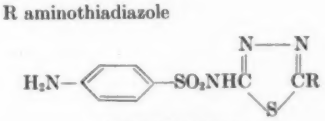


Sulfathiadiazole

a relationship between structure and activity, a series of sulfathiadiazoles was prepared by cyclizing the appropriate thiosemicarbazone to the corresponding aminothiadiazole according to the method of Young and Eyre (*20*) and condensing the heterocyclic amine with the substituted benzene sulfonyl chloride.



Thiosemicarbazone R aminothiadiazole



Sulfathiadiazole

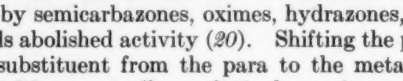
The end product proved to be uninteresting, but impressed by the similarity in structure between the aminothiadiazoles and their thiosemicarbazone precursors, Behnisch and his co-workers (*18*, *19*, *20*, *21*)

tested the latter and found them to be strongly tuberculostatic.

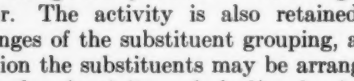
In its activity, tibione occupies a position between streptomycin and PAS. It has had extensive testing in Europe where it has shown itself to be of value in pulmonary tuberculosis and in tuberculosis infections of the mucus membranes, but, like PAS, it is ineffective in miliary tuberculosis and in tuberculous meningitis. In this country it has received relatively limited attention because of its considerable toxicity which manifests itself as gastrointestinal disturbances, anemia, and severe liver and kidney damage.

Scores of variations have been made in the tibione structure in an effort to obtain compounds with increased activity and decreased toxicity. Most of these changes have involved the character and position of the subordinate grouping, since it was early discovered that substitution of the thiosemicarbazone moiety by semicarbazones, oximes, hydrazones, azines, and anils abolished activity (*20*). Shifting the position of the substituent from the para to the meta to the ortho positions generally results in decreasing activity in that order. The activity is also retained through many changes of the substituent grouping, and in the para position the substituents may be arranged in the following order of activity: ethylsulfonyl = isopropyl > amino = acetylamino = dimethylamino > nitro = sulfamyl = methoxy.

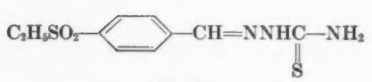
In addition to *p*-acetamidobenzaldehyde thiosemicarbazone (Tb I), the German workers have clinically investigated *p*-methoxybenzaldehyde thiosemicarbazone (Tb II), *p*-ethylsulfonyl benzaldehyde thiosemicarbazone (Tb III), *p*-acetamidobenzyl thiosemicarbazide (Tb V) (the hydrogenated form of Tb I), and the diethanolamine salt of *p*-carboxybenzaldehyde thiosemicarbazone (Tb VI).



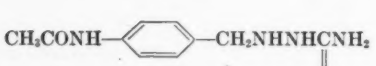
Tb I (Tibione)



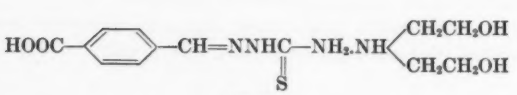
Tb II



Tb III



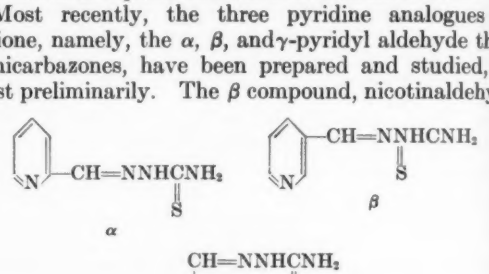
Tb V



Tb VI

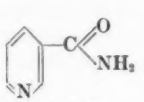
The *p*-methoxy derivative (Tb II) is less active, and the *p*-ethylsulfonyl derivative (Tb III) is approximately as active as tibione. In England, however, the ethylsulfonyl compound (Tb III) is considered to be the most promising (*22*, *23*). The reduced form of tibione (Tb V) has not been sufficiently investigated for a critical judgment, and the carboxy derivative (Tb VI), while somewhat less active than tibione, is better tolerated and is regarded as a worth-while preparation. Moreover, as the only soluble compound of the group, it lends itself to parenteral forms of administration.

Most recently, the three pyridine analogues of tibione, namely, the α, β, and γ-pyridyl aldehyde thiosemicarbazones, have been prepared and studied, at least preliminarily. The β compound, nicotinaldehyde



thiosemicarbazone, was independently prepared in Switzerland (*24*), France (*25*), and the United States (*26*). The findings of the French workers (*25*, *27*, *28*) indicate that the compound is distinctly superior to tibione, and these results have been partially confirmed in this country (*29*). The α compound (picolinaldehyde thiosemicarbazone) and the γ compound (isonicotinaldehyde thiosemicarbazone) were prepared by the author (*30*) and studied by Grunberg and and Leiwant (*29*). The α compound is inactive, and the γ compound has been found to be at least comparable to the β derivative.

Pyridine Carboxylic Acid Derivatives. This last category does not appear in review articles on the chemotherapy of tuberculosis—probably because even its most prominent member, nicotinamide, has been largely ignored by chemotherapists and clinicians in in this country. The activity of nicotinamide was first discovered by Chorine (*31*) in 1945, but the discovery apparently caused no stir, because it was rediscovered in 1948 by McKenzie, *et al*, (*32*), who postulated that tuberculostatic effect was related to the vitamin activity, since any change in structure of the nicotinamide molecule resulted in diminution or abolition of both effects (*33*). Chorine, on the other hand, had shown that nicotinic acid, which had vitamin activity, was not tuberculostatic and contended, therefore, that there was no relationship between the two activities.



Nicotinamide

The tuberculostatic activity of nicotinamide is equal to that of *p*-aminosalicylic acid, but it has not gained favor in this country, because it causes severe liver damage and its strong vasodilator action results in severe flushing. It is, however, being tested more extensively in Europe.

In an attempt to improve the activity, Kushner and his co-workers (*33*) found that replacement of one of the amide hydrogens by an isopropyl, pyridyl, or thiazolyl group resulted in diminished activity, whereas the addition of another substituent, such as chloro, amino, or butoxy groups in the 6 position on the ring completely abolished the activity.

The author (*30*) has prepared and studied a considerable number of compounds closely related to nicotinamide and with two exceptions has found them devoid of activity. The two exceptions are 3-aminoisonicotinic acid and its methyl ester. Both of these compounds are only about one-half as active as nicotinamide and are of no interest clinically, but they do show that tuberculostatic activity in the field of pyridine carboxylic acids is not necessarily limited to derivatives of nicotinamide. In the author's view, this point is of considerable importance.

CONCLUSION

From the foregoing it is obvious that much remains to be done before tuberculosis can be treated as casually as some of the more completely tamed diseases which once took a heavy toll of life. On the other hand, it is equally obvious to those working in the field that now that the start has been made the work will continue until the problem has been solved.

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A FLEXIBLE LABORATORY INFRARED HEATER-DRYER

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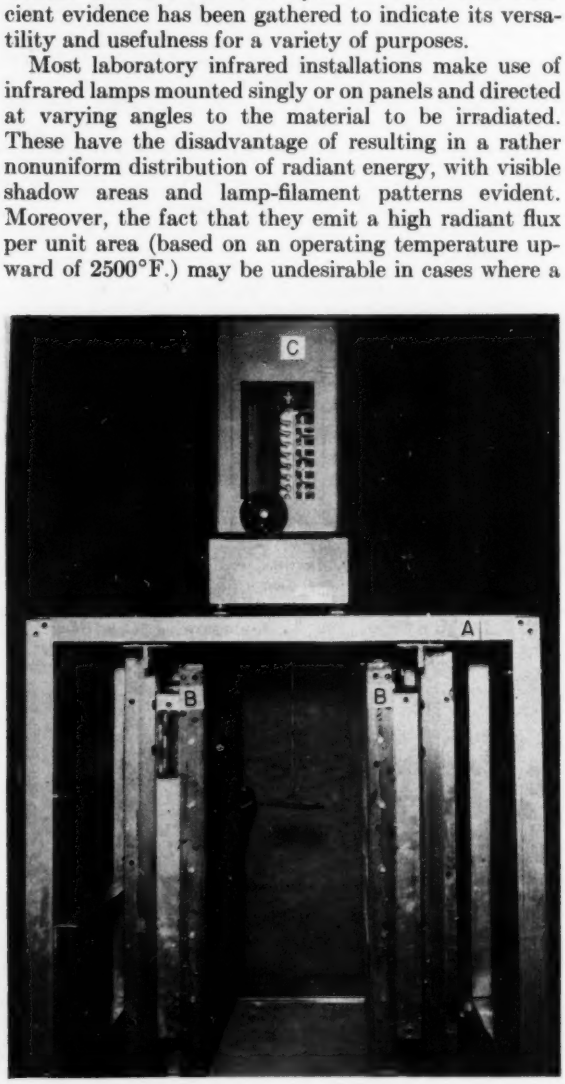
RECENTLY, need arose for a small pilot laboratory set-up wherein fundamental data could be obtained concerning the behavior of materials exposed to infrared radiation under varied experimental conditions. The outgrowth of this need is reflected in the heater-dryer unit described below, which has been in use at Lowell Textile Institute for over a year. In this time sufficient evidence has been gathered to indicate its versatility and usefulness for a variety of purposes.

Most laboratory infrared installations make use of infrared lamps mounted singly or on panels and directed at varying angles to the material to be irradiated. These have the disadvantage of resulting in a rather nonuniform distribution of radiant energy, with visible shadow areas and lamp-filament patterns evident. Moreover, the fact that they emit a high radiant flux per unit area (based on an operating temperature upward of 2500°F.) may be undesirable in cases where a low temperature source with correspondingly longer wave lengths of emitted radiation is required.



As far as the authors know, gas-fired units have not been used for small-scale general infrared dryers, nor can they be feasibly employed where there is any question of "clean heat" or safety involved.

It is believed, therefore, that the type of open-sided unit described in the following paragraphs represents a solution to many of the problems which have vexed laboratory workers.

DESIGN

Framework (*A*). The figure shows a photograph of the unit. The heaters are positioned readily in the vertical or horizontal plane in a framework of right-angle aluminum bars drilled with holes on half-inch centers. This is covered at the top by half-inch plywood faced on both sides by sheets of transite.

Heaters (*B*). As a source of radiant energy fiberglas Superheaters[1] are employed. In these units, heavy Nichrome V wire elements closely woven over and under a mat of fiberglas tapes are covered by fiberglas fabric and backed by $3\frac{1}{2}$ in. of insulation. The entire construction is housed in a rigid aluminum frame. Heaters can be constructed for use on any voltage, any phase, and any frequency, with a maximum operating temperature of 700°F.

A small blower, attached to the back of the heater, passes low-pressure fresh air completely through the heater itself, materially aiding in the removal of steam, vapors, or solvent-laden air for certain types of work.

If desired, the dryer can be converted into a convection oven by adding a horizontal or vertical plywood duct, equipped with baffles and calming section, through which hot air can be led.

Balance (*C*). For quick measurement of weight losses, a rapid-weighing, highly damped balance, such as the Voland Speedigram (capacity 200 g., accuracy 0.0001 g.), is placed on top of the test stand, with a $\frac{1}{16}$-in. aluminum rod and counterweight suspended from the left side of the balance arm. The rod passes through a $\frac{3}{4}$-in. hole in the upper horizontal heater.

From the end of the balance rod a small piece of screening, frame, or other similar device may be hung to support the sample.

Controls. The heaters are maintained at any desired temperature from 120° to 700°F. by a Leeds and North-

[1] Manufactured by and obtainable from Industrial Radiant Heat Corporation, Gladstone, New Jersey.

rup Electromax Controller. This instrument provides automatic proportional-duration action and droop correction, with rate of droop correction proportional to magnitude of temperature departure from the control point. By means of magnetic contactors in the external circuit, the surface temperature of either one or two heaters may be controlled by the Electromax within extremely close limits.

Where a greater tolerance in temperature is no handicap, a less expensive mercury-actuated or simple galvanometric on-off control can be employed, with or without a proportional mechanism such as a percentage timer.

OPERATION

Operation of the heater-dryer is extremely simple, merely requiring the setting of the Electromax to the required temperature and waiting for equilibrium to be reached, as indicated by the steady flashing of the pilot lights on the controls.

For curing, heating, or drying operations, where it is desired to ascertain the magnitude of the rate of weight loss, the sample is suspended from the balance rod on a supporting frame. As heating proceeds the time intervals may be noted for equal weight decrements, or conversely, the amount of weight loss occurring in equal time intervals.

Utilizing the appropriate auxiliary instruments, it is possible to gather data not readily available otherwise; *e. g.*, a watt-hour meter to measure power input, or a thermocouple-potentiometer circuit to measure sample temperature, to name just two possibilities.

EVALUATION

Tests conducted at Lowell Textile Institute with the heater-dryer unit have given satisfactory, reproducible results over a wide range of differing experimental conditions in which the distance between heaters, temperature, air velocity, sample size, position of heaters, etc., were varied.[2]

The versatility of the unit is shown by the fact that, in addition to drying and curing data, the unit will handle all the operations normally performed by an ordinary laboratory oven, such as routine drying of materials and apparatus, bone-dry weighing of crucibles, etc. Moreover, there is a decided advantage in the speed and constancy of operation, the temperature being virtually independent of external conditions in contrast to that in an oven when the door is opened momentarily.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to the Industrial Radiant Heat Corporation, whose generosity made possible the acquisition of the equipment.

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ALICE IN STEREOISOMERLAND

"So many odd reactions,"
Moaned Alice on the eve
Of the Chem. examination,
"They must all be make-believe!"

Then the page in Shriner-Fuson
Flapped and fluttered, faded dim
And the Fieser twins receded
Leaving just their Siamese grin.

Poor old Messers Diels and Alder
Quite diene-less did remain—
Baeyer fought for recognition
And produced a fearful strain.

The alkaloids kept strutting 'round—
The terpenes in a panic;
The methylene ketones ducked out
And hid from Mr. Mannich.

The prim and sec and tert amines
Hatched up a vicious plot:
To scramble the reagents,
Then precipitate the lot.

The mixtures smelled of esters
Till the time of separation,
Then the acid and the alcohol
Popped out in desperation.

The phenyl ethyl side chains
Broke away from carbon five
And chased the histamine around
And raised a frightful hive.

The steroid nuclei collapsed
In shattered broken wrecks;
Their carbonyl and OH groups
Were quite devoid of sex.

The sulfa drugs came marching in,
A most impressive lot,
Until the procaine went to work
And froze them on the spot.

The beta pyrroles turned quite red,
They were a fearsome sight:
"If we just had our alphas on
We'd really look quite white."

Then Alice woke and shrieked aloud
For Brewster and for Beilstein,
For Morton, Gilman—anything,
Yes, even poor old Wertheim.

"I should have taken Music 2
Or something just as nifty;
How can I organize this mess
And synthesize a 50?!"

—Marjorie Rodd

UNDERGRADUATE RESEARCH PROJECTS IN QUALITATIVE ANALYSIS[1]

BRUCE McDUFFIE[2]
Emory University, Emory University, Georgia

ONE of the interesting aspects of laboratory instruction in qualitative analysis is the amazing number and variety of questions that are asked by the students. Granted that these questions often arise from the misreading of directions or from other careless mistakes, many of the questions deal with chemical phenomena that the students, and often the instructor, cannot explain. It is to answer some of these questions, as well as to make improvements in the procedures, that we have assigned projects of a research nature to approximately 175 undergraduates in qualitative analysis during the past four years. This number of students represents about 19 per cent of the total enrollment in the course for that period.

Qualitative analysis at Emory University is a one-quarter course which follows a two-quarter sequence of general chemistry. There are three lectures and two three-hour laboratory periods per week. The laboratory work includes the analysis of solutions for cations (about 13 periods), the analysis of solid salts for anions (about three periods), and the identification of simple salts (about two periods). At present the special research projects are not an integral part of the laboratory work, but are reserved for students who finish the required work ahead of schedule and desire to devote one or two periods to such a project. In a previous year the completion of a special project was incorporated in the regular schedule and required of all students.

A student is encouraged to select a project based on his own observations or on a difficulty that he has encountered with a particular step in the procedure or with a particular unknown. If a student has no suggestions the instructor usually has plenty, from his own observations or from the observations and questions of other students. It is often desirable for several students to work (separately) on the same problem. Once a particular project has been selected, the instructor outlines with the student the objective and the plan of attack, then the student proceeds with the experimental work, taking notes as he goes and conferring with the instructor when the need arises. As the work progresses and new aspects of the problem arise the student often goes ahead on his own, devising new experiments. Finally the student submits a report of several pages consisting of: (1) a statement of the problem, (2) a detailed summary of all experimental work, including usually a table of data, and (3) conclusions or recommendations.

The following list of typical research projects will give some indication of the scope and possibilities of this feature of the qualitative analysis course.

Sodium, Potassium, and Ammonium Ions

- Sensitivity of the flame test for sodium.
- Comparisons of various light filters for the potassium flame test.
- Sensitivity of the ammonium ion test using sodium hydroxide.
- Investigation of the yellow precipitate obtained when the ammonium ion test was performed on a solution containing the cations of Group I.

Cation Group I

- Precipitation of lead chloride under various conditions.

Cation Group II

- Optimum acidity for precipitation of Group II sulfides.
- Use of sodium hydroxide plus hydrogen sulfide to dissolve Group IIB sulfides.
- Effect of nitric acid on the precipitation of lead sulfate.
- Sensitivity of the test for bismuth.
- Study of the detection of cadmium in the presence of copper using the sodium chloride-hydrogen sulfide method.
- Study of the test for mercuric ion with stannous chloride.
- Amount of washing needed to remove chloride ions from arsenious sulfide, prior to the test for arsenic.
- Development of a specific test for arsenic.
- A simple confirmatory test for antimony, based on the reprecipitation of antimonous sulfide.
- Investigation of the red-brown solution formed when silver ion is added to traces of stannous ion.

Cation Group III

- Study of the incomplete precipitation of some Group III sulfides.
- Effect of acidity on the reaction of hydrogen sulfide with ferric solutions.
- Effect of impurities on the color of aluminum hydroxide.
- Study of the wine-red color obtained on dissolving a mixture of hydroxides in chloroacetic acid.
- Observations on the precipitation of zinc sulfide, and possible interferences in the test for zinc.
- Study of the complex formed by chromic ion in solutions containing chloroacetic acid.
- Precipitation of basic cobalt chloride as a test for cobalt.
- Development of a simplified procedure for the detection of manganese and iron.
- A study of difficulties encountered in the test for aluminum with aluminon reagent.

Cation Group IV

- Effect of ammonium chloride and ammonia concentration on the separation of Group IV from magnesium.
- Sensitivity of the procedure for the detection of calcium.

[1] From a paper presented at the 28th Annual Meeting of the Georgia Academy of Science, Athens, Georgia, April 27, 1951.

[2] Present address: Department of Chemistry, Washington and Jefferson College, Washington, Pennsylvania.

Anions

Test for nitrate in the presence of nitrite.
Test for acetate in the presence of iodide.
Occurrence of sulfate ion in lead sulfide unknown.
Occurrence of sulfate ion in sulfite unknowns.
Use of ammonia solutions to separate the silver halide group.
Silver ion as a general reagent for the anions.

Miscellaneous

Quick test for the potency of hydrogen peroxide solutions.
Standard names for the colors of precipitates and solutions.
Qualitative analysis of miscellaneous substances, such as coins, rocks, clay, soft drinks, and vitamin pills.

It has been our experience that students enjoy this taste of research and that it provides a fitting climax to the first year's work in chemistry. Of necessity the unit of work accomplished by any one student will be quite small, but taken together these units of work have formed the basis for many changes in the scheme of analysis and have in several cases laid the foundation for more advanced research. Furthermore, as in all research, students learn the importance and the satisfaction of a systematic and imaginative approach to the solving of problems.

To echo the words of R. E. Kirk: "But is this research? Perhaps not to the teacher, but it is real research to the boy! And it is a real teaching tool!"[3]

[3] KIRK, R. E., J. CHEM. EDUC., 9, 280 (1932).

CHEMICAL PROPELLANTS

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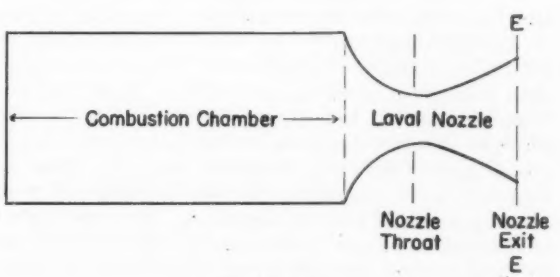
THE chemical propellants form a special class of compounds. Some of the members of this class are usually not considered as being important enough to warrant special discussion in chemistry courses. For this reason it appears to be of interest to present a catalogue of representative chemicals with emphasis on the particular characteristics which make them useful or usable rocket propellants.

In order to understand the function of chemicals in jet propulsion applications, it is necessary to consider the task which the chemicals are called upon to perform. In its bare essentials a rocket rotor consists of a combustion chamber into which the propellants are injected, and from which the products of combustion flow out through a Laval nozzle (see the figure). Experience has shown that nearly complete thermodynamic equilibrium is reached in the combustion chamber and that the expansion of the combustion products through the Laval nozzle from the chamber pressure to the pressure of the surrounding atmosphere is nearly adiabatic.[1]

An analysis of the forces acting on the rocket engine shows that the total thrust F is given by the relation

$$F = \dot{m}V_e \qquad (1)$$

[1] The chamber pressure varies from one rocket engine to another. In liquid-fuel rockets it is usually 300 p. s. i., in solid-propellant motors 1000 to 3000 p. s. i., etc.



Rocket motor

if a number of simplifying assumptions are made.[2, 3] Here $\dot{m}$ is the mass rate of flow of combustion products and V_e is the linear flow velocity in the direction of the nozzle axis at the exit position (*cf.* the plane *E-E* in the figure). The exhaust velocity V_e, in turn, is determined by the enthalpy change during adiabatic expansion from the chamber (identified by the subscript c) to the nozzle exit (identified by the superscript e) according to the relation

$$V_e^2 = 2Jg\Delta H_e^c \qquad (2)$$

[2] TSIEN, H. S., AND F. J. MALINA, *J. Aero. Sci.*, **6**, 50 (1938). F. J. MALINA, *J. Franklin Inst.*, **230**, 433 (1940).

[3] For an elementary account of the "Physics of Rockets" see SEIFERT, H. S., M. M. MILLS, AND M. SUMMERFIELD, *Am. J. Phys.*, **15**, 1, 121, 255 (1947).

where J represents the mechanical equivalent of heat, g is the acceleration of gravity, and ΔH_e^s equals the enthalpy change per unit mass during adiabatic expansion through the nozzle. From equations (1) and (2) it is apparent that we must make ΔH_e^s large in order to obtain a large thrust on the rocket motor per unit weight rate of flow of propellant.

By proper utilization of the equations for conservation of mass, energy, and momentum it can be shown for ideal gases that

$$F/\dot{m}g = \Phi \cdot \sqrt{T_c/\bar{M}} \qquad (3)$$

where Φ is a function only of γ, *viz.*, of the effective ratio of the specific heat at constant pressure to the specific heat at constant volume during expansion, T_c represents the temperature in the combustion chamber, and $\bar{M}$ is the average molecular weight of the combustion products during expansion through the Laval nozzle. In general, both γ and $\bar{M}$ change during expansion because chemical changes are taking place while the gas is being cooled from the chamber temperature T_c to the exit temperature T_e. The chamber temperature T_c can be calculated for any given chemical propellant system by well-known thermodynamic methods.[4] Since the specific heat ratio γ does not vary greatly from one chemical propellant to another, it is apparent from equation (3) that the selection of suitable propellants to yield large thrusts per unit weight rate of flow of propellant involves the selection of systems yielding high chamber temperatures T_c and low average molecular weights $\bar{M}$.

The requirement of small values of $\bar{M}$ is met in practice by using reducing compounds containing a great deal of hydrogen as well as relatively light oxidizers, preferably compounds of fluorine and oxygen rather than of chlorine, bromine, and the like. In general, the heat released and hence the value of T_c will be large for those chemical reactions leading to the production of compounds with large negative standard heats of formation from reactants with small negative or even positive standard heats of formation. Here the standard heat of formation is defined in the usual way, *viz.*, as the heat evolved (standard heat of formation is negative) or absorbed (standard heat of formation is positive) when the given compound is formed at 298.16°K. and 1 atm. from the elements in their respective standare states.

The preceding considerations have emphasized the fact that large thrusts per unit weight rate of flow can be obtained from chemical compounds which produce large values of $\sqrt{T_c/\bar{M}}$. This parameter may therefore be considered to be a convenient factor for the evaluation of performance of given chemical propellants. In practice, operational problems, other than performance, will also have to be evaluated.

The particular chemical compound which is most useful for a given propellant application depends upon the device which is to be built. A complete survey of propulsion units and of the chemical compounds used as driving fluids is outside of the scope of the present discussion. Instead, representative chemicals which have been used or may be useful for the more important propulsion units are listed below.

Chemicals Which May Be Used as Propellants

A. Oxidizers in Bipropellant Systems

nitric acid	nitrogen tetroxide
oxygen	chlorine trifluoride
ozone	hydrogen peroxide
fluorine	nitrogen trifluoride
fluorine oxide	bromine pentafluoride

B. Reducing Materials in Bipropellant Systems

hydrogen	gasoline
ammonia	kerosene
hydrazine (N_2H_4)	aniline
hydrazine hydrate ($N_2H_4 \cdot H_2O$)	methyl alcohol
diborane (B_2H_6)	ethyl alcohol
tetraborane (B_4H_{10})	propyl alcohol
pentaborane (B_5H_9)	acetylene
borazole ($B_3N_3H_6$)	ethylene
borimide ($B_2(NH_3)_3$)	methane
aluminum borohydride ($Al(BH_4)_3$)	other hydrocarbons
disiloxane ($(SiH_3)_2O$)	other alcohols
disilane (Si_2H_6)	aldehydes
trisilane (Si_3H_8)	ketones

C. Monopropellants

nitromethane	hydrogen peroxide
dinitroethane	hydrazine

D. Gas-generating Compounds

hydrazine	hydrogen peroxide

E. Water-reactive Chemicals

aluminum borohydride ($Al(BH_4)_3$)	potassium
lithium	lithium hydride
sodium	sodium hydride

F. Fuels for Ramjets

Any suitable liquid reducing compound	carbon
carbon-metal mixtures	boron

G. Oxidizers in Solid Composite Propellants

potassium perchlorate	ammonium nitrate

H. Fuels in Solid Composite Propellants

Polymers containing mostly carbon and hydrogen

J. Double-Base Propellants

Homogeneous colloidal mixtures of roughly 50 per cent nitrocellulose (containing in the neighborhood of 13 per cent N) with roughly 50 per cent nitroglycerin. In some double-base propellants the amount of nitroglycerin is reduced to about 20 per cent and such substances as dinitrotoluene, potassium nitrate, etc. are added to act as stabilizers, plasticizers, flash suppressors, coloring or darkening agents, etc.

Bipropellant mixtures consisting of a liquid oxidizer and a liquid reducing material are used extensively in rocket propulsion work. In general, satisfactory performance cannot be expected between any oxidizer listed in Group A and any reducing compound listed in Group B. A complete quantitative analysis of optimum

[4] See, for example, WENNER, R. R., "Thermochemical Calculations," McGraw-Hill Book Co., Inc., New York, 1941, Chap. XI.

performance requires study of the thermodynamics of combustion. Practical utility depends on such factors as ease and speed of combustion, propellant density, toxicity, coolant characteristics, etc. It is, however, evident that the reducing and oxidizing compounds which have been chosen as liquid propellants generally yield combustion products of low molecular weight at high temperatures, thus assuring large thrusts per unit weight rate of flow of propellant.

A propellant is useful as a monopropellant for rocket applications if it can be made to burn with the evolution of heat and the production of low molecular weight decomposition products. Gas-generating compounds must have similar properties although it is generally desirable to have maximum production of gases at relatively low temperatures.

Water-reactive chemicals are substances which react exothermically with water with the production of large volumes of gas. They are used in such devices as the hydroduct and hydropulse.[5]

Ramjets, which do not carry their own supply of oxidizing agent, are best powered by the combustion products formed as the result of chemical reaction between a liquid reducing compound or a simple metal or nonmetal and atmospheric oxygen or nitrogen.

Composite solid propellants differ from double-base propellants by being more or less heterogeneous. Thus they consist of a nonuniform mixture of oxidizing and reducing materials. Solid double-base propellants, on the other hand, consist of homogeneously compounded materials, the discontinuities in physical and chemical properties being of colloidal dimensions.

The more important characteristics of desirable liquid propellent chemicals are summarized below. The reasons for emphasizing the listed characteristics are, in some cases, closely related to the results obtained from a study of the thermodynamics of combustion. On the other hand, some of the desirable physical characteristics follow rather obviously from handling or cooling requirements in liquid-fuel rocket engines.

A list of desirable physical and chemical characteristics of propellants for use in propulsion units, other than liquid-fuel rocket engines, can be prepared by rather obvious changes of the material which follows.

Desirable Physico-Chemical Properties of Propellants Used in Liquid-Fuel Rocket Engines

(1) Small negative or preferably positive standard heats of formation of the reactants.

(2) The reaction products should have low molecular weights and large negative heats of formation. If conditions (1) and (2) are met, then the reaction products will consist of low molecular weight compounds at high temperatures, thus assuring good performance.

(3) The propellants should have large densities in order to minimize the dead weight of storage tanks.

(4) The oxidizers and reducing agents are best handled as liquids. Hence it is desirable to obtain propellants which are normally liquid in the operating temperature range of service units (*i. e.*, from about −40 to +60°C.). For substances such as liquid oxygen and hydrogen special cooling units must be provided. This refrigerating equipment represents added dead weight which the propulsion unit must carry and is warranted only in the case of very high energy propellent mixtures.

(5) In normal propellant operation the combustion chamber temperatures may get excessively high. Hence it is necessary to provide special cooling equipment for the chamber walls. Cooling may be accomplished by forced convection involving passage of oxidizer and/or reducing agent through coils enveloping the chamber. In extreme cases this cooling technique is inadequate and it is necessary to resort to sweat cooling which is accomplished by passing a small amount of one or both of the propellants through small passages in the chamber wall, thus using the heat of vaporization as well as the specific heat of the oxidizer and/or reducing agent in order to cool the chamber wall. It is apparent that successful cooling can be accomplished the more readily the higher the specific heat and/or the heat of vaporization of the material involved. Hence it is customary to choose, if possible, at least one of the components of a bipropellant system with a high specific heat and/or large heat of vaporization.

(6) Since it may be necessary to store the propellants for long periods of time before use, good propellants should have high storage stability, *i. e.*, they must not decompose or change chemically in any way during storage so that their use as a propellant is impaired.

(7) Since propellants are chemicals which have to be handled by service personnel it may be desirable for some applications to use propellants of relatively low toxicity. Actually the art of propellant design has advanced at the present time to the point where practically every useful bipropellant component is toxic or represents a handling hazard for other reasons. As the result of this development it has become important to educate service personnel on the proper handling of dangerous chemicals.

(8) For large-scale use it is, of course, imperative that propellants which are readily available and preferably also of low cost are employed. In practice this last requirement is inessential since experience has shown that rare and expensive chemicals which are needed in large quantities usually become cheap and readily available in the course of time.

(9) The bipropellant mixture in a liquid-fuel rocket should be spontaneously combustible with minimum time lag. Spontaneously combustible propellants are said to be *hypergolic* whereas nonspontaneous[6] propellants are said to be *nonhypergolic*. The time lag or ignition delay is the period of time preceding steady-state combustion. It is measured empirically and is a function of physical factors such as injection methods, motor configuration, etc., as well as of the chemical constitution of the propellant mixture. Long ignition delays may lead to the accumulation of large amounts of propellant in the combustion chamber before vigorous exothermic reaction occurs and initiates steady-state combustion. The accumulation of excessive amounts of propellant, before steady-state combustion occurs, is usually accompanied by severe initial shock and very high initial pressures which may lead to rupture of the combustion chamber.

(10) The reaction products should not be excessively corrosive or form solid deposits thereby leading either to increased or decreased nozzle throat diameters. In the former case steady-state combustion may cease altogether or else occur at such low pressures as to impair over-all performance. Nozzle plugging, on the other hand, may lead to an excessive increase in chamber pressure followed by rupture of the combustion chamber.

(11) For application to guided missiles the exhaust gases should not interfere with the guidance method which is being used.

[5] The reader interested in a more complete discussion of jet engine design is referred to ref. (2) and also to the book "Principles of Jet Propulsion and Gas Turbines," by M. J. Zucrow, John Wiley & Sons, Inc., New York, 1948.

[6] Abbreviation for "nonspontaneously combustible."

PAUL PASCAL

CLÉMENT DUVAL
The Sorbonne, Paris, France
RALPH E. OESPER
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PAUL PASCAL, whose "Traité de chimie minérale," popularly known as "Pascal," has made his name familiar to chemists almost everywhere, was born at St. Pol (Pas-de-Calais) on July 4, 1880. He graduated, first in his class, from the École normale supérieure in 1905. From 1905 to 1908 he taught at the Lycée at Douai, and then even before defending his thesis (Docteur ès Sciences, 1909), he was named (1908) *maître de conférences* at the University of Lille, where he taught applied chemistry. He was at this school until 1928, when he was called to the Sorbonne, where he has occupied successively the chairs of applied chemistry, mineral chemistry, and general chemistry. He has also taught at the École centrale, the École normale supérieure, and the École normale de filles at Sèvres. His retirement in 1950 has not diminished his activity; he still continues his researches and participates in the work of important committees.

Paul Pascal

At the outbreak of World War I he served in the infantry on the Belgian front, but in 1915 he was sensibly recalled to make use of his scientific and technical abilities. He was given charge of the powder works of Angoulème, of the manufacture of guncotton, synthetic nitric acid, yperite (mustard gas), panclastite. A staff of 185 worked under his direction. For these services, he was awarded the Legion of Honor *à titre militaire* in 1917.

Professor Pascal has published many books. His famous "Traité de chimie minérale," was composed with 65 collaborators. The 13 volumes appeared in rapid succession between 1931 and 1933. He himself wrote 862 pages, including the sections on bromine and iodine (which served as models for his associates), nitrogen, ammonium salts, and rhenium. Some volumes of this monumental work are now out of print. Though not entirely without errors, it continues to render tremendous service to its many users. For the students in his courses he published: "Métallurgie" (1921); "Synthèses et catalyses industrielles" (1921, 1924, 1932); "Explosifs, poudres et gaz de combat" (1925, 1932); "Acides minéraux" (1936); "Métalloïdes" (1937); "Cinétique" (1938); "Thermodynamique chimique" (1932); "Equilibres chimiques" (1939); "Structure et liaisons atomiques" (1943); "Liaisons interatomiques" (1944); "Liaisons interioniques et intermoléculaires" (1944). In addition to these texts, whose titles themselves display the wideness of his competency, he has collected some of the ideas developed in his courses into "Chimie générale" (2 volumes issued). It has been said that the two volumes still in preparation are being awaited "with impatience as though they were the romances of Alexandre Dumas." They are written in a really clear and attractive style; they take account of the most recent discoveries and ideas, and they do not hesitate to guide the reader to the base of the mountain of difficulties.

Professor Pascal's pedagogical record is important. Some 60 engineers have completed theses under his direction, and seven of his students are teaching in institutions of higher rank. He is universally looked upon as an example of what a professor should be: a good teacher delivering his lectures in a clear and attractive fashion, possessed of a wide culture, indefatigable, and always ready to serve. His countenance, whose lineaments have retained their youthful appearance to a remarkable degree, is usually graced with a smile. All in all, he gives a perfect picture of a courteous and cultured gentleman.

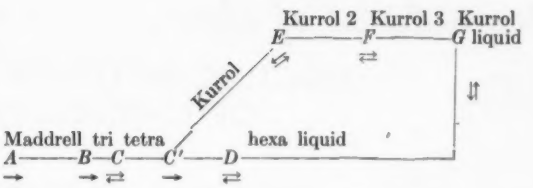
Although his scientific activities have covered a wide range, the most important labors can be put into three categories: (*a*) magnetochemistry; (*b*) metaphosphates; (*c*) nitrogen and its derivatives.

(*a*) In 1907 Langevin and Weiss had just proved

that diamagnetism is a general property of matter and that the paramagnetic molecule functions as a permanent magnet with a multiple moment equal to that of the magneton. By measuring the magnetic susceptibility of a wide variety of materials, inorganic and organic, Pascal provided qualitative evidence regarding the nature of complex salts and the condensation of colloidal hydroxides, and derived some additive laws which gave an insight into the structure of molecules. He has postulated that the molecular susceptibility of a compound equals the sum of the atomic susceptibilities plus a correction term designed to take account of the particularities of the molecular edifice. With respect to its paramagnetic qualities, oxygen does not conform to the additivity law; in combination it yields different values according to how it is bound to its neighboring atoms. Double bonds lower the diamagnetism, but this property is increased by a tertiary carbon or quaternary atom adjacent to an oxygenated function or an aromatic nucleus. The effects of tertiary carbons nullify each other when the molecule is symmetrical with respect to the oxygen, as in isoamyl oxide. Pascal made an extended study of keto-enol forms, discovered some quinoid structures, and proved the configuration of certain oxyacids of sulfur and phosphorus. He also established a law which is nicely illustrated by a classic experiment on the simple and complex salts of iron: in a series of complexes it is possible to follow in parallel fashion the attenuation of certain analytical characteristics and the paramagnetic properties of a metal, and thus demonstrate the fact that the magnetic properties are connected with the ionic state of the element or with the mode of arrangement in its complexes.

(*b*) Pascal's earliest inorganic researches dealt with the alkali ferro- and ferripyrophosphates. The former are highly reducing in character; the latter represent perfect complexes. Later he discovered intensely colored (red) ferriammines, some uranyl pyrophosphates with masked sodium, and complexes with triazine tricarboxylic acid.

At that time the history of the metaphosphates was quite obscure. It was filled with contradictions and exclusively chemical methods did not permit the members of the series to be individualized. Pascal was the first to prepare sodium metaphosphate ($NaPO_3$) not polymerizable by heat. He then studied the products obtained by heating a monometallic phosphate and established the following connective scheme with respect to all the materials he studied, with the exception of some dimetaphosphates, which were not isolated until later. It should be noted that the tetrametaphosphates can undergo a double evolution according to whether they are heated slowly or rapidly.



The temperatures at the points $A, B, C, C' \ldots$ are shown in the following table, which refers to the sodium and potassium metaphosphates. Some of these transition points are also given by thermal analysis of these systems.

	A	*B*	*C*	*C′*	*D*	*E*	*F*	*G*
Sodium salt	250°	505°	607°	...	640°	595°	725°	810°
Potassium salt		170°		320°	960°	420°	505°	835°

(*c*) Except for factory traditions, no data were available prior to World War I, regarding the manufacture of nitric acid, its distillation, recovery, etc. Pascal studied the $NO_2 \rightleftarrows HNO_3$ equilibrium; he showed that the peroxide does not have a condensation state above the dimer; he explored the $H_2O - HNO_3$ azeotropic mixture between 40 and 870 mm. Subsequently, he was able to prove that in the case of the sulfo-nitric mixture, the maximum in the boiling point disappears when the sulfuric acid reaches 65 per cent. For military needs, he had found that the peroxide can be produced by treating spent acids from the nitration of cotton with sulfur. He also studied the fluidity of guncottons. For the scientific operation of factories, he measured the specific heats, heats of mixing, and densities of nitric-sulfuric mixtures. He also studied their attack on lead, steel, and aluminum.

Pascal is still busy with such problems as the industrial synthesis of benzene from acetylene, the distillation of schists and lignites, the analysis of fatty substances, and the nitration of naphthalene. Recently, a magneto balance was constructed in his laboratory which permits the determination of susceptibilities at various temperatures. Valuable discoveries can be expected from this instrument.

Professor Pascal's honors include the Houzeau Prize in 1917, the Lacaze Prize in 1930. He was named Correspondant of the Académie des Sciences in 1927, and was elected titulary member of the Chemistry Section in 1945. He received the rosette of the *Officier* of the Legion of Honor in 1949. He is still an active member of numerous national committees including Comité consultatif de l'Enseignement supérieur, Défense nationale, Comité des Poudres, and Commission interalliée des Industries de l'azote et de la potasse.

Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA[1]

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THE University of Southern California is the largest private university west of the Mississippi. In contrast to many of the other large schools, however, its endowment is small, giving an income which is negligible in comparison with tuition receipts. Founded in 1880 it has, therefore, gone through several periods of rapid development and others of severe retrenchment as the economic and cultural conditions of the state fluctuated. By being alert to the needs of the population and emphasizing the personal touch and quality of instruction, it has been able, however, to reach its present state of development.

While chemistry has been an important part of the science curriculum since the founding of the university, masters' degrees having been granted since 1892 and occasional doctorates in chemistry since 1932, the real development of the chemistry department did not begin until a short dozen years ago when A. B. Burg came to a four-man department in which there were only a dozen graduate students in 1939, and became its chairman two years later. Today there are 14 regular faculty members and an active graduate school of some 60 selected graduate students and postdoctoral fellows, coming from most states of the Union, Canada, and abroad, mainly from India, England, and Holland.

The faculty group is very active and unusually young, their ages averaging about 36, ranging from 27 to 46. Their training and experience are quite varied. The 14 men received their bachelor degrees in 11 different schools (Chicago claims three and Wisconsin two) and their Ph.D. degrees in nine different institutions (Chicago and Harvard claiming three each and Berkeley two). They taught or did postdoctoral research at 10 schools other than those that granted their degrees (Harvard and Stanford each claiming two) before coming to U. S. C., and average over one year of industrial experience. Their research interests range from synthetic organic to synthetic inorganic chemistry, from the structure of crystals to that of colloids and of solutions above the critical temperature, from radiochemistry to rheology. None is, however, interested specifically in analytical chemistry and as a result advanced degrees are granted only in the fields of colloid, inorganic, organic, and physical chemistry, over 40 publications dealing with these fields having appeared last year from the department.

Part of the teaching load is carried by postdoctoral lecturers on temporary appointment who spend one or a few years at the University to gain experience before proceeding to other posts. Most lecturers divide their time equally between research and teaching.

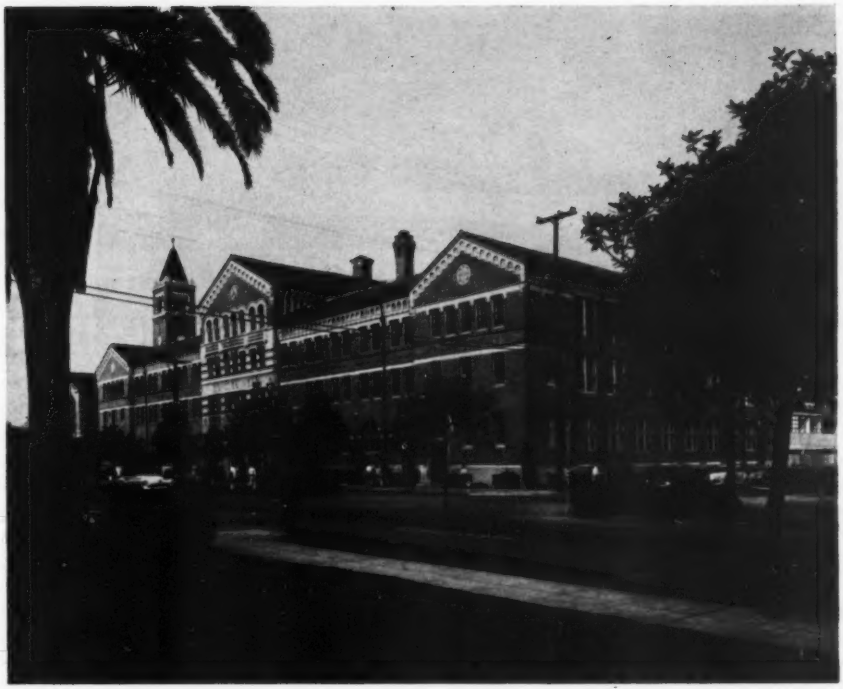
Graduate students are admitted on the basis of promise for advanced work as evidenced by their undergraduate grades and letters of recommendation. It has been the policy of the department to advise students intensively, to screen them early and vigorously, and to grant both the M.S. and the Ph.D. titles as research degrees only after full demonstration of merit. The M.S. degree thus is not a "consolation prize" but a recognition of definite achievement beyond the B.S.

After being admitted, the new graduate student consults with one of three members of a faculty committee which deals with all new students, who learns of his particular problems and explains what will be expected of him. The student then takes a three-hour orientation examination on the basis of which he is advised by the full committee about his chances of success and the best ways of preparing to meet the next hurdles. Frequently students are advised at this point to begin by taking undergraduate courses in physical or organic chemistry to make up deficiencies.

Before the end of their first term all new students are required to take three "background" examinations covering organic, physical, and inorganic-analytical chemistry at an advanced undergraduate level. The equivalent of a strong B performance in each examination is required for passing. The student may attempt these examinations twice but if two are passed on the first attempt he is required to repeat only one. At this point, student mortality is over 50 per cent and less than 20 per cent pass all three on the first attempt.

[1] This is the first of a series of articles, sponsored by the PSACT, describing chemical education in western colleges and universities.

These examinations have been found very effective in eliminating at an early stage, before a large investment of time and effort has occurred on the part of either students or faculty, those who are unable to show the thorough grasp of fundamentals which is considered a necessary prerequisite for successful advanced work. On the other hand, those students who pass these examinations have been found, in most cases, to proceed from there on without having to spend time reviewing basic material so that an atmosphere more conducive to creative research prevails in the student body.



Science Hall

This houses the main activities of the chemistry department as well as several of the other science departments.

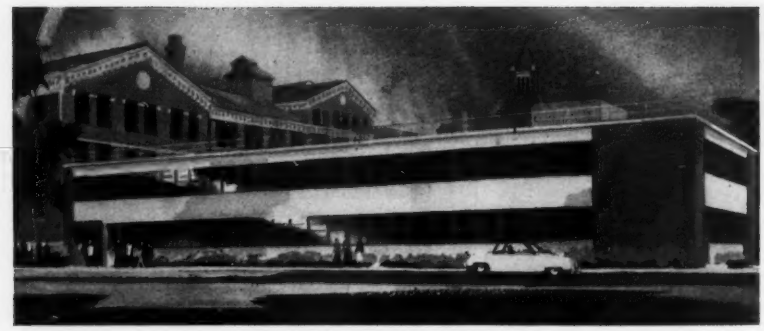
As a rule, students are admitted to research only after passing the three background examinations, or on a probationary basis after passing two, although research may be commenced immediately on entrance on a petition basis if an individual has special qualifications. A thesis showing the ability to obtain publishable results is required for the M.S. degree, which is granted after satisfactory completion of 28 units of study and a final oral examination dealing mainly with the thesis and the courses taken in the major field. The examining committee also recommends whether the student should or should not be discouraged from continuing for the Ph.D. degree.

The work of Ph.D. candidates (whether they have an M.S. degree or not) is closely followed by a committee of at least three faculty members which meets twice a year with the student to discuss the progress of his research and related matters in order to evaluate his creative imagination, critical facility, and ability to express ideas, as well as his progress in research and in the independent study of his field. These qualities, including the capacity to do independent work, are believed to be even more essential than successful course study in fitting the person for work in responsible positions, be it in industry or in teaching. After each meeting, the candidate is informed of his progress toward the degree.

After at least three semesters of research, and only if his progress has been satisfactory, the student may present himself for the "qualifying" examination which is oral and which deals with his research and any topics connected with it, with questions given him two weeks in advance and to which he has prepared written answers, and with original "propositions" submitted by him. In this way the candidate is tested in his ability both to handle established topics and to originate significant new ideas, but quite purposely a rehash of course work is avoided. The examination is taken after the student has had a chance to mature and establish himself in his chosen field but again before an excessive investment of time and effort has occurred. After passing this examination, the student completes his research and finally defends his Ph.D. dissertation in a final formal examination.

Graduate courses include some which are more or less standard, such as thermodynamics, advanced organic, and advanced inorganic, in which the student acquires the advanced tools of his profession, as well as courses which are built around the special fields of various faculty members, such as radiochemistry, high vacuum techniques, etc., in which more specialized knowledge is explored up to the present-day borders of science.

Seminars and informal colloquia serve as group meetings in which current literature and work in progress in each field are discussed among faculty and graduate students. Work completed in the department and talks by outside speakers are presented at a weekly "research conference" attended by both graduate and advanced undergraduate students. Phi Lambda Upsilon, Iota Sigma Pi, Sigma Xi, and the American Chemical Society Student Affiliate societies provide additional opportunity for formal and informal



The New Building for Organic Chemistry

contact between students of all fields and the faculty.

An unusual feature of the graduate program is the curriculum leading to an M.S. degree in industrial chemistry. It is designed for graduates in chemical engineering or in chemistry who wish to obtain additional training in the other field without satisfying its full undergraduate requirements.

All graduate students who desire it receive financial support after passing the qualifying examinations and the more promising ones even upon entering. This support comes from teaching "laboratory assistantships" and "associateships" provided by the University, and research assistantships and fellowships provided by a number of industrial firms, the Office of Naval Research, the Atomic Energy Commission, the U. S. Public Health Office, and the Research Corporation. However supported, all work done in the department deals only with fundamental problems and is fully publishable.

A faculty committee and an all-University office help in the placement of students in full-time, part-time, or summer positions. Arrangements are made for interviews on campus with representatives of the larger companies who visit the department regularly.

The department has the policy of not giving its students a "third degree." It believes that in the five or six years of study leading to the B.S. and M.S. degrees a student, if he is of a Ph.D. caliber, has received from this faculty all that he could gather and should be exposed to a new and different atmosphere at another school. This policy leads to the loss of some of the most promising students but is believed to be of distinct benefit to them.

In its undergraduate program, the department serves the needs of (1) relatively small groups of chemistry, chemical engineering, petroleum engineering, geology, and physics majors and a larger group of premedical students, (2) engineers other than chemical or petroleum engineers, and (3) liberal arts students with no technical interests. There are three corresponding freshman courses: a professional 10-unit lecture and laboratory course with emphasis on qualitative concepts of equilibrium and structural considerations based as far as possible on laboratory experiments; a rigorous terminal 8-unit lecture and laboratory course which has already been described in THIS JOURNAL,[2] and a terminal 2-unit lecture and demonstration course emphasizing aspects of chemistry of greatest importance to the general student not specializing in the sciences or engineering. This latter course may in the future be incorporated in a general science course.

Only students from the first course are admitted to more advanced ones. The same semester-course in quantitative analysis, emphasizing quantitative aspects of equilibrium, is taken by all advanced students, but courses in organic chemistry in which theoretical correlation of reactions is stressed, and in physical chemistry in which problem work is emphasized, have additional laboratory periods for chemistry majors. Premedical students generally terminate their study of chemistry after organic, and chemical and petroleum engineers after physical chemistry, while chemistry majors continue with courses in instrumental analysis, chemical literature, and electives such as organic qualitative analysis, phase rule, elementary colloid, and some of the specialized graduate courses. This curriculum gives the student the basic tools for adapting himself to an industrial position and enough of a survey of the field to whet the appetite and provide a perspective for those who may wish to continue in graduate work.

The best undergraduates may conduct research under a faculty member's close supervision. This new experience gives the student an excellent indication of his suitability for research and graduate work. While some find that they are better adapted to other aspects of a chemical career, others are most stimulated by this work, and several have succeeded in their senior year in competing work which was published in journals of the American Chemical Society.

This fall a new wing to the main Science Building will be completed to house the teaching and research activities of the organic group. This will relieve considerably the present congested conditions of the department and will make possible better housing of many instruments, such as the recording X-ray spectrometer, infrared spectrometer, mass spectrograph, ultracentrifuge, light-scattering, and conductivity equipment, some of which are now kept in temporary structures put up in 1947 to accommodate the postwar flood of undergraduates.

For several years the department has been publishing two brochures, one describing its faculty, publications, and fellowships; the other, detailed degree requirements. These brochures are gladly sent to interested persons upon a request which should be addressed to Robert D. Vold, who became Head of the department last year on a system of rotation.

[2] MYSELS, K. J., AND C. S. COPELAND, J. CHEM. EDUC., 28, 165 (1951).

Report of the

NEW ENGLAND ASSOCIATION
OF CHEMISTRY TEACHERS

A QUAKER VIEW OF THE SECONDARY-SCHOOL CHEMISTRY COURSE[1]

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As I understand it, the purpose of this symposium is to investigate the role which chemistry may play in general education. Such an investigation presupposes a definition of the term "general education," but such definitions are hard to get. It has doubtless been the experience of most of us that the professional educators (and by this term I mean the teachers of courses in education), when asked to clarify the term, take off into flights of fancy which are decidedly annoying to those of us who are used to dealing with tangible things like test tubes and crucibles. Yet the theorist in education and the teacher of chemistry may find common ground in an expression which is bound to crop up somewhere in the discussion—"the education of the whole child." There is no doubt that the tendency to consider the student as a whole and to endeavor to contribute to that whole in every course to which he is subjected is a step in the right direction.

Last October at a conference of the Educational Records Bureau in New York City, I heard Dr. Frank Bowles of the College Entrance Examination Board speak on "Crystal Gazing and the College Boards." In his address, the main purpose of which was to stress the growing significance of the Scholastic Aptitude Tests, he drew a picture of the breakdown of the subject-matter divisions, and he predicted that in the not-too-distant future the applicant will be offering for admission to college such subjects as "communications among peoples." As near as I could gather, a course of this sort would include everything from reading and writing to radio, radar, and television; and physics and chemistry as such would be no more. Most of us are teaching in institutions which rather pride themselves on the "middle-of-the-road" policy which they follow. We like to say that we "skim the cream" from the new while we retain the best of the old, or that "our feet are on the ground." Granted, we hope, that comglomerations such as Dr. Bowles suggested are still far away, we need to recognize that the modern trend in teaching is toward the education of the whole child, and we need further to consider what our chemistry courses can contribute to the picture.

During many meetings of this Association we have had occasion to discuss the problem of the content of the college preparatory course in chemistry. I can remember rather vividly holding forth on this subject, with a warmth which matched the outside temperature, at the Tenth Summer Conference at the University of Maine. At that same summer conference action was taken which led to the appointment of a committee which formulated a syllabus for the college preparatory course. This syllabus was officially adopted a year later. While there are undoubtedly points in it with which each of us would disagree, it represents, for the most part, through the considered opinion of a representative group of our membership, what we as an Association feel should be the content of the course which prepares for college. What is there left to say except, "Read the syllabus"? I should like to consider, therefore, an aspect of the secondary-school course in chemistry which I have heard discussed much less frequently, and one which I believe that all of us will agree is vastly more important—the intangible contributions which the study of chemistry can make to the development of the whole child, and what we can include in our courses which will contribute to this development.

A basic tenet of the Quaker faith is summarized in the words, "There is that of God in every man," and this doctrine of the "Inner Light" has motivated the Quaker way of life—our worship, our social program, our daily living, and our educational theory. The belief that in every man there resides a bit of the divine is certainly not unique to Quakers, but underlies much of the religious thought of our day. Friends are probably better known for it than most religious faiths because, in our quiet way, we make more noise about it. How-

[1] Contributed to the symposium on the Content of the General Course at the 13th Summer Conference of the NEACT, University of Rhode Island, Kingston, Rhode Island, August 21, 1951.

ever, all of us, as teachers of chemistry, can and should aid in the fanning of this divine spark, and it is quite as much our privilege to contribute in this manner to a better world as it is to invent plastics, synthetic rubber, or an atom bomb. I am, of course, talking about, the "building of character," an expression which I loathe because it has been so bandied about that it reeks with sentimentality.

I am thinking, first of all, of our opportunity to train students to be people of decision. A lot of the trouble in this world of sin and sorrow comes from what my grandmother used to call "shilly-shallying." So many people lack the ability to view a situation from all angles, to make a decision in regard to a course of action, and then to proceed. Too many of us allow others to make our decisions for us, either because we are too lazy to do the investigating necessary for a decision, or because it is the course of least resistance. How many of us are Republicans because our fathers were? How many, when election day comes along, say, without having done a bit of investigation for ourselves, "The issues are so complicated that I just couldn't make up my mind, so I voted the straight ticket"? What can we do to help our students to learn how to make decisions based on facts? How can we train our students in what Professor Ralph Barton Perry of Harvard University calls the "art of decision"?

There are numerous ways which will doubtless occur to each of you. I am thinking especially of the role which the laboratory work might play. For the most part our so-called laboratory experiments are mere cook-book exercises. I do not know the answer to the problem which I am posing, but I do wish that there were some way in which the student could be encouraged to plan out his own course of procedure. I wish that each laboratory exercise might be done because of a desire either to confirm something read in the text or to pursue some suspicion which may have flashed into the mind. If the student could then plan out and do a series of experiments to gather his confirming data or to back up his suspicion, he ought to get infinitely more out of his precious laboratory hours. The teacher would act in an advisory capacity, keeping the pupil away from explosive situations and helping to point the way when the going gets too rough.

To be specific: in the usual laboratory experiment on the preparation and properties of oxygen, we tell the student to mix and heat certain weights of potassium chlorate and manganese dioxide. In some schools the material, all weighed and mixed, is handed to the pupil. After he collects the gas, he performs certain stunts according to directions. It seems to me that the vigorous student ought to ask himself whether other oxygen-containing compounds upon heating will also give up oxygen. He ought to be given the opportunity of planning what compounds might be used and how to treat them. We wish, of course, for him to observe for himself the properties of the gas under discussion. Every beginning student should have the fun of burning iron picture wire in oxygen. Why not have a tank of oxygen in the laboratory and give everyone as many bottles of the gas as he needs for making the various tests which we feel will be necessary for him to become acquainted with oxygen, but when it comes to generating the gas, let him work out several techniques of his own. Of course, he may instead think of some novel way to demonstrate some property of oxygen. If he does, well and good. The important thing is for him to become accustomed to making a plan and then carrying it out, basing the conclusions which he makes on data which he has thus obtained.

I can think of two important objections to any such course of procedure. Sad but true, there are some students who will almost never be able to think up a course of action and then follow it. They are the "all we like sheep are gone astray" group to which the prayer book refers, the people who would infinitely rather follow than lead. For them the traditional laboratory exercise will be intellectually satisfying, if it satisfies at all. Yet these are the people who, more than their brighter or less lazy fellows, need the type of work I have been describing, and I suspect that even the poorest of them has an occasional glimmer which, if seized and acted upon, might lead to something approximating a decision in regard to a course of action.

The teacher, however, will probably offer greater difficulty. Frankly, as I contemplate running a laboratory along these lines, I have the feeling that I should be sitting on a not-very-small volcano. How we could ever keep it from being a chaotic situation and how we could ever preserve our own sanity I do not know. In addition, those of us who have been in the college preparatory game for some time are so accustomed to the thought that our students *must* have notebooks in which are recorded 25 to 30 experiments that the thought of spending as much time on one subject as this method would require takes on the quality of a nightmare. Of course, many colleges (Mount Holyoke and Wellesley, for example) no longer ask for the number of experiments performed, trusting in the records of the graduates of a school to indicate the adequacy of its courses, but some boards of admission still demand a certain number of experiments or at least ask how many have been done. I cannot help wondering how such a Board of Admission would react if I were to write in the column labeled "Number of Experiments Performed" a number like 10, and then to add, "but they were *real* experiments."

An unsuccessful experiment, planned and carried out by a student, like a negative result, can make a contribution, since it may help to make the student realize that he is not infallible, that he doesn't know it all yet, that just because he has made a plan it won't necessarily work. It is my firm belief, however, that laboratory experiments such as I have outlined, carried to a successful conclusion, can give a child a certain feeling of reliance on his own ability to plan, to do, to observe, and to conclude. It could develop habits of thinking that will contribute toward considered decisiveness of action in places other than the laboratory.

A second aspect of the "Inner Light" to which we may make a definite contribution is the love of truth. Most of us, as we think back to our childhood, will realize that love of the truth has been a gradually growing thing in our lives, that a sense of responsibility for the truth and a hatred of what is false is an acquired trait, and one which has grown and should continue to grow as each day passes. We tell children that they must not lie, but most of them will until they come to a realization of what the truth is through some vital experience of it. I can remember some of the whopping lies which I told as a child, not that they would do me any good or get me out of anything, but simply because peoples' astonished reactions were so perfectly delightful! If there is anything in the universe which is real, it is the truth, and anything which we can do to make it fascinating and vital is a contribution to the individual and to the whole world.

Here, again in the laboratory, through the quantitative experiment, we can relate facts which are experienced to the intangible realities. In performing a simple experiment like finding the percentage of oxygen in potassium chlorate, the student should get a feeling of respect for a set of figures. If he weighs out roughly 3 g. of potassium chlorate on Harvard trip scales, then places his material in a crucible weighed to estimated thousandths of a gram, reweighs the crucible and the potassium chlorate, and deduces the corrected weight of potassium chlorate, he begins to get a little perspective about what figures mean, of what an accurate weighing is, and, more important, of what it isn't. A little of the challenge of ever increasing accuracy makes itself felt. The fact that his results agree roughly with those of other experimenters can and should make the student aware that the data with which he is constantly being presented are based upon the truthful observations of others. As he works with experiments of this sort, he may come to have a feeling of respect for what he has taken so casually and to sense one aspect of truth.

Closely allied to the love of the truth and stemming from it is a sense of honesty. The recent publicity in regard to cheating in certain of our higher institutions of learning has greatly shocked us all, partly, I suspect, because it has forced us to face a situation the existence of which we have all known but have been reluctant to admit. Cheating is just as real a problem in secondary school as it is in college, and we cannot help wondering what is wrong with an educational system which apparently does so little to develop love and respect for the truth. Surely, where the truth is not revered honesty will not exist.

If in our income-tax returns we include income derived from extra-curricular activities like tutoring merely because we don't dare do otherwise, let us face squarely the fact that while we may be prudent in so doing, we are not being fundamentally honest. We need to recognize that honesty based on fear of being caught is not honesty at all but mere expediency; that real honesty has a very different motivation.

However, dishonesty may be partly a habit, and in our zeal for accuracy we need to be very careful that we do not encourage its formation. As high-school teachers we are not trying to train analytical chemists, and the quantitative experiments which we include have for their purpose the development of certain techniques and mathematical relationships, not the obtaining of better and more accurate data. Hence, I believe, our emphasis should be on the interpretation of results, not on the results themselves. Certainly, all other aspects being equal, the student who gets the best numerical data should get the best grade, but undue emphasis on accuracy alone will pressure the weakling into errors far worse than poor results! For this reason we should always insist on the calculation of the percentage of error and on its interpretation. There should be a list of logical explanations for the error. It is not enough to say, "I must have weighed wrong." Instead, at least, the pupil should say that the original weight of his crucible must have been too heavy, perhaps because he forgot to dust off the pan or because there was material on the outside that burned off, or some other such plausible explanation. It is interesting to see that often the student can diagnose his difficulty and upon repetition of the exercise can obtain more satisfactory results. A good interpretation of error is of far more value to the beginning student than a result that by good luck "hits it right on the nose." I wonder if an intelligent understanding of possible and probable pitfalls isn't half the point of a quantitative experiment at the secondary-school level.

The use of significant figures and the insistence that measures be recorded to the proper degree of accuracy is another lesson in honesty. If the weighings on a set of scales can be read accurately to hundredths of a gram and estimated to thousandths, then we should never accept a reading in less than three decimal places. If a volume can be estimated to tenths of a milliliter, then we should refuse to accept readings which record either hundredths of milliliters or whole milliliters. Experiences like these make the student really aware of what we mean by honest observations. Every time he makes observations with as great accuracy as possible, he cannot help but have a greater sense of what the truth is.

In assigning problems to be prepared as homework we encounter again the problem of honesty. I think that it is just as well to face the fact that students simply *will* work problems together or compare answers when they are done, making proper revisions after the conference period! For this reason I never forbid working together and I never give any credit for problems done outside of class. This latter technique is not popular at first, but I find that my girls soon bow to the inevitable. Frequently, to discourage working together, I give the answers to a set of problems. All my girls soon learn, however, that one thing is certain: there will be a quiz which *will* count for credit and will be based on the type of problem on which they have been working outside. It doesn't take too long for them to realize that if they are getting too much help from their friends I am pretty apt to find it out. Such a quiz must be honest on the

teacher's part, with enough straightforward material like the assigned problems so that the faithful and conscientious student will be able to demonstrate that he knows how to do the problems assigned. Tricky problems have their place, but not in quiz material testing ability to do assigned work.

As we consider honesty, is it too much of a truism to add that we need not expect from our students any greater degree of honesty than that which we ourselves show? Every teacher of a college-preparatory chemistry course knows that, in order to prevent us from cramming our students, the College Entrance Examination Board does not publish its examinations. A year ago I heard of a man (not one of our members) who teaches in one of our large New England cities. Before the examination, he instructed each of his students to memorize the general content of a certain section of the paper. From their reports he was able to reconstruct practically the whole examination. Guided by it he may have been able to offer better instruction in taking the examination given last March. We may frown upon the ethics of such a procedure, but I feel a much deeper concern in regard to what such an act did to the ethical standards of the students. How much could *he* contribute toward the building in his pupils of a sense of what is inherently honest and good?

The last intangible which I wish to discuss is one which, as I have been thinking over these remarks, I have found most difficult to put into words. A part of the heritage of every chemistry student should be a respect for the unknown and a willingness to acknowledge the reality of things for which we have no explanation. To the student in secondary school the recognition of this reality is especially important. He is at an age when he doubts everything which he cannot prove with the facts which he has, and such doubts worry him since they are frequently concerned with his religious experience. The transition from the anthropomorphism of childhood to an adult religious faith based upon individual experience and thought is difficult at best. It is a transition never made by some and imperfectly made by most of us. I have found that my own girls seem to get a good deal of comfort from the realization that the revelation of truth to the individual, as to the race, is an unfolding thing which is constantly going forward as we have the courage and persistence to pursue it. I believe that our students could get a far keener sense of this continuing revelation through the honest searching of human minds if we had time to do more work in the history of chemistry which, in our rush to "cover ground," we have to neglect. They get some idea of it as we discuss the atom, beginning with Dalton, continuing through the Periodic Table, atomic structure, radioactivity, and atomic energy. They glimpse it when we teach the law of conservation of energy and the law of conservation of mass and then point out that we must now modify the two laws into one. At some stage in the course it is easy to hint that the student has been accepting on faith a good many things which he himself cannot prove—for example, the theory of the atom, and that it doesn't trouble him because no one has ever seen an atom. Sometime, somewhere, somehow our courses in chemistry should rise above equations, formulas, processes and logical deductions, and give our students a sense of the majestic orderliness of the universe, of the beauty of its dependability, and of our unique place in the scheme of things.

I am thinking of a verse in the New Testament which says: "For what shall it profit a man if he shall gain the whole world, and shall lose his own soul?" (St. Mark VIII, 36). It is not, I believe, irreverent to apply this thought to our own discussion. For what *is* the profit to a student if he is able to write formulas, balance equations, do problems, recite preparations and properties, and perform complicated laboratory procedures if he has not at the same time touched the soul of chemistry; if his contacts with the course and with us have not made him better able to gather data on which to make considered decisions, if they have not given him a passion for the truth and if he has not become aware of the promise held out to him in the ever-continuing revelation of truth to man.

To the Editor:

On page 556 of the October, 1951, issue of the JOURNAL OF CHEMICAL EDUCATION, J. C. Hackney comments critically on one of the series of exercises presented for illustrative purposes in my July, 1951, paper, "Evaluation of Achievement in Chemistry." While it is probable that on the level of high-school or elementary college chemistry the better students would respond to these items in the way intended, superior students whose understanding of oxidation, reduction, and neutralization includes the concepts listed by Hackney could be in difficulty. His criticism admirably supports statements made elsewhere in my paper: "In concluding this discussion of various types of objective exercises, the importance of careful evaluation and editing of exercises prior to use should be stressed. After

exercises have been written they should be carefully checked for accuracy of phraseology and correctness of the key."

MAX D. ENGELHART

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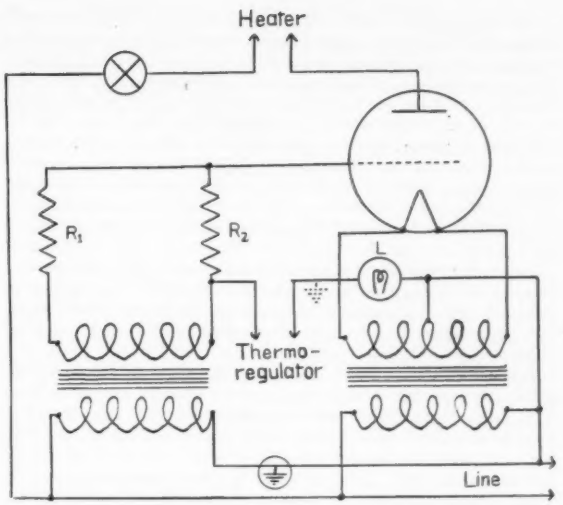
CHICAGO, ILLINOIS

To the Editor:

The simple electronic relay described by John J. Pitha (J. CHEM. EDUC., **28,** 429 (1951)) is a device which fills a long-felt need. However, Mr. Pitha's use of a battery, which is bulky and needs occasional replacement, can be eliminated and the device made entirely self-contained. Indeed, the 3C23 tube works better when "triggered" with alternating current. At 120 volts on the cathode, 3 volts or more are needed for the grid bias. The most compact way of obtaining this would be to add an extra winding to the filament transformer. A few turns only of fine wire would be needed, as no more than 50 milliamperes is carried, and this could be poked in over the secondary without disassembling the transformer. It is more convenient, but slightly more expensive, to use a small auxiliary transformer giving about 6 volts. A bell-ringing transformer is suitable.

The writer is using at the present time a relay with the latter arrangement, the circuit diagram for which is shown in the figure. R_1 and R_2 are two ordinary half-watt radio resistors with the approximate values of 20,000 and 100,000 ohms, respectively. The specifications are otherwise identical with Mr. Pitha's. The two transformer primaries are connected in parallel, and of the two possible ways of doing this only one will work, because of phase considerations. The simplest means of determining the right way is to leave the 6-volt transformer leads unsoldered when building the relay, simply twisting them in place. After completion the relay is tested, and if it does not work these leads are reversed. They may then be soldered and taped.



The circuit shown was designed for use with a Cenco mercury thermoregulator, which has a metal mercury reservoir. This means that the regulator is necessarily grounded, at the point shown by the dotted ground symbol in the figure, so that plugging in the line with the "live" side towards this point would cause a short circuit. To prevent this the lamp L was connected between the lead from the regulator reservoir and the filament transformer center tap. This lamp is a 110-volt, 7-watt pilot light. If it lights when the power is switched on the plug should be reversed. The circled ground symbol indicates merely on which side the grounded side of the power line should be connected. The resistance of the lamp does not affect the operation of the relay.

DUNCAN G. FOSTER

SWARTHMORE COLLEGE
SWARTHMORE, PENNSYLVANIA

Recent Books

• INTRODUCTORY COLLEGE CHEMISTRY

Harry N. Holmes, Professor of Chemistry, Oberlin College. Fifth edition. The Macmillan Co., New York, 1951. viii + 594 pp. 178 figs. 2 color plates. 14.5 × 22 cm. $4.75.

As WITH previous editions, this book is designed for introductory college courses in general chemistry. Principles of chemistry are emphasized, there being a good balance between theory and practical applications. The book is written in an interesting manner, with the historical material woven into the discussions without overemphasis. Repeated revisions since 1925 have resulted in a style which will appeal to the student, is easy to read, and at the same time sufficiently rigorous to meet the demands of any groups of students.

The fifth edition involves considerable revision, especially as regards the size and structure of atoms, the early introduction of the periodic table accompanied by a thorough discussion, the introduction of hydrogen as the first element to be studied rather than oxygen, a more complete discussion of atomic energy and fission, and the early study of metals to support qualitative analysis in the laboratory. The above changes bring the book in line with present trends in the teaching of general chemistry.

The distinction between ionic and molecular compounds is presented in Chapter 3. Quantitative concepts and problems involving chemical changes are introduced before symbols, formulas, and equations. The laws of definite composition and combining proportions are first discussed, leading deductively to the concept of molecular weight, the quantitative significance of the chemical equation, and the determination of chemical formulas from analytical data. The above quantitative aspects of general chemistry are introduced in the first five chapters of the book. The first elements studied as a group are the halogens, followed by the alkali metals. Fifty pages are devoted to organic chemistry.

An excellent diagram is given of the atomic pile. Interesting features of the book include the method of presenting the uses of elements and compounds in tabular form, the discussion of alloys, the applications of colloidal phenomena, and the chapters on nutrition, chemotherapy, and plastics.

Few errors were noted. The equation $NaCl = H^+ + Cl^-$ is given on page 192. Some topics are discussed rather briefly; such as the solubility of water-insoluble hydroxides in acids, hydration of ions, freezing-point lowering, and boiling-point elevation. In view of present knowledge it seems that the law of conservation of energy, given on page 7, could have been stated in terms of mass and energy; especially since the statement of the law is thus qualified in the discussion which follows. Purely numerical quantities are used in the solution of most problems. The use of dimensions may help the student to better understand the problem and its solution.

PAUL R. FREY

COLORADO A AND M COLLEGE
FORT COLLINS, COLORADO

● ADVANCES IN RADIOCHEMISTRY

Engelbert Broda, **Dozent in Physical Chemistry in the University of Vienna. Cambridge University Press, London, 1950. x + 152 pp. 16 tables. 14.5 × 22.5 cm. $2.75.**

THIS small book reviews progress in radiochemistry in what might be called its modern era—the period beginning with the discovery of the neutron and the large variety of artificial activities in mid 1930's. The material is organized under the following chapter headings: Introduction, The Role of the Chemical Differences between Isotopes in Radiochemistry, The Distribution of Tracer Quantities between Solids and Liquids, Tracer Quantites in Gases, The Electrochemistry of Radioelements, The Production of Radioelements by Nuclear Synthesis, The Chemical Aspects of Nuclear Fission, New Radioelements of Special Interest, Specific Radiochemical Effects, Chemical Excitation Due to Nuclear Reactions, and New Developments in the Technique of Radiochemical Measurement.

Each chapter consists of a terse factual review of the subject, carefully documented with references, averaging more than 10 per page of text. With the obvious exceptions of the first two chapters and the last, the subjects appear to be completely covered and therefore this book will find use as a key to the literature for those already acquainted with the general features of the subject.

RUSSELL R. WILLIAMS, JR.

UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

● COLLEGE CHEMISTRY

Herman T. Briscoe, **Professor of Chemistry, Indiana University. Fourth edition, Houghton Mifflin Co., Boston, 1951. vii + 564 pp. 285 figs. 29 tables. 19 × 25 cm. $4.50.**

PREVIOUS users of Dean Briscoe's very substantial text will be pleased with its new clothes. Binding, paper stock, and typography are excellent and of modern style. The double-column format has been retained.

When a general-chemistry text revision is shorter than its predecessor that is news—good news—and this fourth edition is 22 pages shorter than the previous edition. It is unnecessary to discuss in detail the contents of a book that has had such wide usage for so long. The principal changes found in this edition consist of some minor changes in order of topics, the rewriting of certain sections, some deletions of obsolete processes, and the addition of a new chapter on natural and synthetic organic products. Former Chapters 8 (Molecular Weights) and 9 (Atomic Weights and Combining Capacity) are combined into one new Chapter 8 (Molecular and Atomic Weights). Former Chapters 11 (The General Classification of Compounds) and 13 (Classification of the Elements) have been rearranged and the material appears for the most part as Chapter 10 (The General Classification of Elements and Compounds). The discussion of nuclear reactions has been extended to include the transuranium elements and tracer techniques. Newer applications of antibiotics and silicones, and other similar topics, have been introduced at appropriate places. The discussion of combining proportions has been rewritten and simplified.

The modifications of this well received text should make for smooth presentation of the material. Previous users of this text will welcome this revision and it should make many new friends.

FREDERIC B. DUTTON

MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

● GENERAL COLLEGE CHEMISTRY

Joseph A. Babor, **Professor of Chemistry, and** ***Alexander Lehrman,*** **Associate Professor of Chemistry, College of the City of New York. Third edition. Thomas Y. Crowell Co., New York, 1951. xvi + 800 pp. 166 figs. 9 tables. 16 × 23.5 cm. $5.**

THIS is the second revision of the well-known text with the same title, written in 1929 by Professor Babor and revised in 1941 by the present authors. As in the former edition the text is said to be designed primarily for the more able and scientifically minded students.

The general plan of the book is much the same as the second edition with changes as needed to bring it up to date, including a chapter on nuclear chemistry. The first 20 of the 42 chapters in the book are given over to a consideration of gases, atomic-molecular hypothesis, energy in chemical reactions, chemical equilibrium, atomic structure, electron distribution and valence, solids, solutions, ionization, and ionic equilibria, with the usual chapters on hydrogen, oxygen, water and hydrogen peroxide, and the atmosphere included. The next nine chapters take up the descriptive chemistry of the nonmetals, including a chapter on oxidation-reduction and one on colloid chemistry. This is followed by 10 chapters discussing the common metals, a chapter on the electrochemical cell, one chapter on nuclear chemistry, and one each on organic chemistry and nutrition.

The revised edition is up to date in its treatment of atomic structure concepts and their applications. Electron distribution in the orbits is clearly shown by figures and tables although no mention is made of subshells. Mass number is used in a table on page 130 without being defined elsewhere in the book.

The figures in the text are accompanied by brief descriptions as well as titles to provide the reader with sufficient detail for them to be self-explanatory without reference to the text. Many of the illustrations are three dimensional drawings. A few drawings of molecular structure are included.

The revision contains extensive exercises, numerical problems with answers, and a reading list at the end of each chapter. The reading list includes references not only to books but to numerous journal articles including many in the JOURNAL OF CHEMICAL EDUCATION and a few in such magazines as *Fortune, Chemical Age,* and *Chemical Products.* Sometimes the author and title of the journal article are given, as well as the volume and page, but the practice is not uniform.

Although the stoichiometric problems are well treated with numerous illustrations and problems, the space and importance

given to other types is very brief. For example, calculation of pH from hydrogen ion concentration is described at length but only a few pages are used to describe the calculations from ionization constants and solubility products. Only three numerical problems involving solubility product are given. Nothing is said about activity coefficients, even though they are included in the authors' shorter book, "Introductory College Chemistry," second edition.

The appendix is in twelve sections, which include many useful tables such as metric system, vapor pressure, solubility product, freezing mixtures, bead tests, alloys, solubilities, isotopes, discussion of mathematical operations, and four-place logarithm and antilogarithm tables.

The many years of experience of the authors in presenting general chemistry has resulted in a well-written book. It should be given careful consideration by anyone selecting a text for a course in general chemistry in which it is desired to devote a large part of the first semester to the study of the principles of chemistry. In its up-to-date revision it will be especially welcomed by the teachers who have used the earlier edition.

L. REED BRANTLEY

Occidental College
Los Angeles, California

● THE SOLUBILITY OF NONELECTROLYTES

Joel H. Hildebrand, Professor of Chemistry, University of California, and *Robert L. Scott,* Assistant Professor of Chemistry, University of California. Third edition. Reinhold Publishing Corp., New York, 1951. x + 488 pp. 138 figs. 110 tables. 16 × 23.5 cm. $10.

The time is ripe for a textbook on the very important solubility phenomena. This volume, although it is written as a monograph on solutions, is an excellent textbook for a graduate course in solutions. It does suppose a good basic knowledge of classical thermodynamics and the ability to handle the mathematics used in thermodynamical calculations. Students taking a fundamental course in thermodynamics get for the most part a smattering of solution chemistry and this book is an extension of the thermodynamics of solution and the thermodynamics is well done. Most of the nonelectrolyte solution chemistry acquired by a student of chemistry comes mainly from a course in phase rule which is usually empirical and the question of thermodynamics is more or less divorced from the discussion.

Graduate students majoring in physical chemistry and chemists in general, in this reviewer's opinion, are not "educated" until they have mastered the fundamental principles of the physical chemistry of solutions. Courses are given in this subject in most graduate schools but without a textbook. This volume will fulfill that need.

The book has 23 comprehensive chapters embodying all types of nonelectrolyte solutions from the ideal case to solutions of high polymers. The second edition lacked the story of high polymer solutions which are so important at the present time.

These chapters on solutions deal exclusively with the thermodynamic properties of mixtures and pure substances in phases in which the molecular environment is the same in all directions. The authors have extended the thermodynamic discussion of solutions to the interface between the main masses of two solution phases. Also included in this new monograph is a chapter on polarity which very fittingly precedes one on solvation. These two chapters and the one pertaining to hydrogen bonding are as important to the organic as to the physical chemist. Each chapter which appeared in the second edition has been expanded both from the standpoint of data and from theoretical considerations.

The authors are to be congratulated for this timely and much needed work in the field of physical chemistry. It is clearly written and as far as the bibliography is concerned, the authors did not "miss a trick."

FREDERIC C. SCHMIDT

Indiana University
Bloomington, Indiana

● CHEMISTRY . . . KEY TO BETTER LIVING

Edited and produced by the staffs of *Chemical and Engineering News* and *Industrial and Engineering Chemistry.* American Chemical Society, Washington, D. C., 1951. xxi + 244 pp. Illustrated. 24 × 31 cm. $4.

This volume might well be used as a style manual or model for those engaged in preparing books or specializing in graphic art. But it is far more than that. It is primarily a history of chemistry in America during the past 75 years and of the interrelation of the American Chemical Society and the American chemical industry as they have developed and progressed side by side during that period. A series of papers on chemical progress during the 75 years since the founding of the A. C. S. reviews the development of chemical science and its industrial applications and discusses the part the A. C. S. and its divisions played in the advancement of chemical knowledge and skill. This series was organized to subdivide chemistry roughly into the fields covered by the divisions of the A. C. S. and the order of presentation follows approximately the chronological order in which the divisions were established. These histories are all written by outstanding leaders in the fields covered.

A special feature of the book is "The First 75 Years" by Anthony Standen. This story, copiously illustrated, and written in the inimitable style of the author of "Science Is a Sacred Cow," relates, as its title indicates, the significant developments of the first 75 years of the A. C. S. and particularly the role the Society and its members played in the industrial chemical growth of the nation. A picture-caption story graphically presents this same 75-year period. Then there are sections written by well-known authorities who give a glimpse at our science and civilization. They discuss contemporary problems as the scientist, philosopher, business executive, and teacher envision them.

In addition to the excellent make-up, arrangement, and typography, the volume is arrestingly bound in cobalt-blue cloth, lettered in genuine gold leaf with the A. C. S. emblem attractively displayed on the backbone and outside front cover. This book should be a "must" in the library of every chemist and chemical engineer who is proud of his profession and his professional society, their beginnings, development, and progress during 75 years, and their limitless opportunities. It should be a valuable reference in the libraries of industrial concerns, research laboratories, and educational institutions.

● THERMODYNAMICS OF IRREVERSIBLE PROCESSES

S. R. de Groot, Professor of Theoretical Physics in the University of Utrecht. North-Holland Publishing Co., Amsterdam; Interscience Publishers, Inc., New York, 1951. xvi + 242 pp. 4 figs. 16 × 23 cm. $4.

Apparently this book is intended for an advanced graduate course. Its author assumes for his readers a knowledge of higher mathematics and a wide familiarity with thermodynamics and statistical mechanics. Although Professor de Groot modestly claims to be writing only a review of the recently developed theory of irreversible processes, a glance at the bibliography reveals that he himself must have made important contributions to the subject.

The first paragraph of the preface follows. "During the last ten years a macroscopic theory of irreversible processes has been developed into a more or less complete system. This theory is based on a double foundation formed by considerations which were put forward already before the systematic theory was formulated. In the first place the introduction of nonequilibrium thermodynamical functions gave rise to the setting up of an entropy balance equation in which the notions of entropy flow and of entropy production occur. In the second place the theory is rooted on the Onsager reciprocal relations, macroscopic equalities, which are founded on the property of microscopic reversibility."

The chapter headings are: (1) Introduction, (2) The Onsager

Reciprocal Relations, (3) Systems of a Single Component, (4) Heat Conduction, Electrical Conduction, and Relaxation Phenomena in Continuous Single Component Systems, (5) Discontinuous Systems without Chemical Reactions, (6) Discontinuous Systems with Chemical Reactions, (7) Continuous Systems (Diffusion, etc.), (8) Thermo-electricity, (9) Chemistry, (10), The Stationary States, (11) Further Discussion on Foundations.

Although the mathematical treatment in parts of the book probably is beyond most of us chemists, the presentation has been arranged to permit omission of 41 out of 82 sections. The 41 sections are those on the statistical basis of Onsager's reciprocal relations, and on other advanced or specialized topics.

W. F. LUDER

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BOSTON, MASSACHUSETTS

● TECHNIQUE OF ORGANIC CHEMISTRY. VOLUME IV: DISTILLATION

Edited by *Arnold Weissberger*, Eastman Kodak Co., Rochester, New York. Interscience Publishers, Inc., New York, 1951. xxvii + 668 pp. 294 figs. 98 tables. 16 × 23.5 cm. $14.

THIS book is a comprehensive, not to say encyclopedic, coverage of distillation theory and procedures. Following an extensive discussion of distillation theory, the main subdivisions are: "Ordinary fractional distillation," "Extractive and azeotropic distillation," "Distillation of liquefied gases and low-boiling liquids," "Distillation under moderate vacuum," "Distillation under high vacuum," and "Sublimation." In most sections there is a separate discussion of apparatus and procedure. Both large-scale commercial distillation and small-scale laboratory operations are described, in most of the book the emphasis being on precise laboratory work.

The sections of the work have been prepared by a number of authorities yet they have produced a unified whole. Descriptive material is excellent, and sometimes deceptively simple appearing—an account of elementary apparatus, which one is tempted to call the same old stuff, being followed by a plunge into theoretical consideration of the most advanced sort.

References are cited in great detail, the summaries being well digested and given in sufficient detail so that in many cases reference to the original article will not be needed.

To everyone who wants to understand distillation thoroughly, particularly the research worker wishing to solve a difficult separation problem, and the chemical engineer, the book should be invaluable.

CHARLES D. LOWRY

EVANSTON, ILLINOIS

● LABELLED ATOMS

***Raymond Glascock.* Sigma Books, Ltd., London, 1951. 227 pp. 59 figs. 9 tables. 13 × 19 cm. $1.25.**

THE use of tracer isotopes as an investigative technique has been rather completely summarized in this handy sized book of somewhat more than 200 pages. The reader will do well to have an elementary background in both chemistry and physics before starting on the book. In the event that he has forgotten many of the details of his background, however, he will still profit by the reading, as the author has explained almost everything with very great care and clarity. A historical approach has been used throughout. Thus one is introduced to the techniques under circumstances of minimum complexity.

The author begins his work with a discussion of the structure of the atom and the nature of radioactivity. Radioactive decay series and the nature of isotopes are explained. The use of tracer isotopes in solving simple chemical problems, such as in testing the Arrhenius theory of ionization, is taken up before proceeding to the more extensive biochemical applications. A clear distinction is shown between problems which are sometimes handled by tracer isotope techniques but which could also be solved by chemical methods, and problems which could not be solved by any method were it not for the tracers. A different type of distinction is made between experiments which are important because they demonstrate the value of a technique and those that are important because of the conclusions.

Some space is devoted to the production of artificial radioactive and stable isotopes and to their incorporation into the desired compounds. The use of inactive carriers when the labeled substance is present in minute quantities is explained.

The book contains excellent line diagrams some of which are used to augment descriptions which are perfectly clear even before one looks at the diagrams.

Good generalizations, made wherever possible, help the reader to organize the varied topics which are included. Most of the experiments described are in the fields of medicine and nutrition, but a few applications in inorganic and analytical chemistry are included as well as some in plant physiology and the value of fertilizers.

The early construction of the Geiger counter is described and illustrated, along with several recent types of counters designed for special purposes. The Nier mass spectrometer is similarly described and illustrated although, surprisingly, the earlier spectrometers have not been included. The sensitivity of the mass spectrometer is compared with that of the counter.

Although bearing the publication date of 1951 the book evidently went to press before the author learned of the discovery of the man-made elements of atomic numbers 97 and 98, berkelium and californium. He stops his periodic table with curium of atomic number 96. This omission in no way detracts from a book which is a delightful summary of an important technique. The conclusions from biochemical experiments in which the technique has been utilized are well summarized but, of course, only as completely as can be done in a small volume.

CATHARINE BERGEN

STATE TEACHERS COLLEGE
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● CLASSICAL MECHANICS

***H. C. Corben*, Associate Professor of Physics, Carnegie Institute of Technology, and *Philip Stehle*, Associate Professor of Physics, University of Pittsburgh. John Wiley & Sons, Inc., New York, 1950. xvii + 388 pp. 22 figs. 14.5 × 22 cm. $6.50.**

THE classical theory of mechanics has received more attention than any other branch of physics and its fundamental position with respect to all other physical theories has long since been taken for granted. Even though its principles have undergone radical revision through relativity and quantum theory, a thorough understanding of its basic ideas is still an essential preparation for all serious research in modern pure and applied physics and chemistry. What is the justification for the appearance of a new work in this well-worn field? The authors of the volume under review aim to stress once more the basic assumptions of classical mechanics and in addition to point out clearly its limitations. They are principally interested in the subject as a background to quantum mechanics and their choice of presentation and subject matter is governed accordingly.

A rapid review of the topics treated will document the statement just made. These include Lagrange's equations, scattering problems, linear vector spaces with applications to small oscillations and the kinematics of rigid bodies, transformation theory of mechanics, and the Hamiltonian equations, as well as an introduction to the special theory of relativity. The degree of attainment required of the student who would study this material with profit is that represented by strong intermediate courses in mechanics and electricity of university grade, or preferably a good introduction to theoretical physics on the elementary graduate level. The rather sparing use of figures will remind some readers of the celebrated boast of Lagrange in his "Mechanique Analytique."

Since the book contains no discussion of the mechanics of con-

tinuous media it will not provide an adequate preparation for students who desire to acquire competence in mechanics for use in such important modern fields as acoustics and elasticity. Even for those readers planning to go on to quantum mechanics some elementary considerations of quantum theory would have made the volume much more helpful. However, in the rather severely limited realm to which they have restricted their attention, the authors have produced a substantial and valuable work.

R. B. LINDSAY

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

● RADIOCHEMICAL STUDIES: THE FISSION PRODUCTS. BOOKS 1, 2, AND 3

Edited by *Charles D. Coryell*, Department of Chemistry, Massachusetts Institute of Technology, and *Nathan Sugarman*, Institute for Nuclear Studies and Department of Chemistry, University of Chicago. Division IV, Plutonium Project Record, Volume 9, National Nuclear Energy Series. McGraw-Hill Book Co., New York, 1951. lxv + 2086 pp. 687 figs. 275 tables. 15.5 × 23.5 cm. $18.50 per set.

THESE three books provide a scientific and technical record of research carried out on the nation's wartime Plutonium Project from May, 1942 to June, 1946 by members of the fission-product groups at Chicago, Oak Ridge, Ames, Berkeley, Bloomington, Hanford, and Los Alamos. The task of the fission-product radiochemistry groups included the isolation and characterization of more than 100 new nuclear species formed in uranium and plutonium fission, extending over that section of the chemist's periodic table from zinc ($Z = 30$) through gadolinium ($Z = 64$). When one recognizes that the chemical behavior of many of these elements, such as zirconium, niobium, molybdenum, ruthenium, and the rare-earth elements, had not been investigated extensively prior to 1942 and that the separation of these elements in a state of purity was often difficult to achieve, one begins to realize the magnitude of the task. Moreover, these new nuclear species had to be isolated in tracer amounts from highly radioactive and chemically complex mixtures and subjected to radiochemical purification involving separation factors as large as a billion, sometimes by remote-control processes and often within times of the order of seconds or a few minutes in contrast with separation times of the order of an hour often encountered in conventional analytical separation methods.

The 336 research papers making up the three volumes cover not only the radiochemistry of the fission products, as the title of the volumes indicates, but also details of instrumentation and specialized techniques, as well as information on the physics and technology of the fission products and nuclear chain reactions. The topics covered are perhaps best indicated by listing the subdivisions of the volumes: Part I, Counting Techniques; Part II, Chemical Studies at Tracer Levels; Part III, Remote-Control Techniques; Part IV, Studies of the Fission Process; Part V, Radioactivity of the Fission Products; Part VI, Radiochemistry of the Fission-Product Elements; Part VII, Special Studies of Gaseous Fission Products; and Part VIII, Radiochemical Studies of Other Activities. The editors have written an introduction to each of these parts in order to correlate the papers and acquaint the reader with the terminology and methodology required for an understanding of the papers in each subdivision. Each paper is preceded by an abstract.

The volumes are completed by four appendixes: A, Fission-Product Decay Chains; B, Fission Yields; C, Nuclides Formed in Thermal Fission; and D, Author Index. An adequate subject index is included. The numerous figures have been well executed and most of the papers are well supported by tables of data. The volumes have been lithoprinted and are attractive in format and sturdily bound.

There is inevitable overlapping of subject matter among some of the papers, and some conflict of results reported in different papers. However, the editors have carefully added footnotes as well as references to the postwar literature so as to assist the reader in obtaining the best evaluation of the work reported. Cross references have been liberally used. Thus, the over-all result is to give the reader not only the benefit of the more recent results and their interpretation, but also a historical survey of the progress of this research during the years of World War II.

These volumes should definitely be of considerable value to nuclear chemists and nuclear physicists, analytical chemists, chemical engineers, and reactor technologists, and to all who are interested in one of the more fascinating aspects of the nation's atomic energy program. Especially valuable to radiochemists are the numerous detailed methods for the separation of tracer amounts of radionuclides. Although most of these methods relate to separations from reactor-slug solutions and fission-product mixtures, the methods should be helpful to the radiochemist in working out his own separation problems.

The editors undertook a monumental task in compiling these volumes and deserve the gratitude of their fellow scientists for the excellence of their product. This reviewer can well imagine their sighs of relief when their work was completed and the sincerity of their thankfulness which seemingly prompted the date of the volume editors' preface· Thanksgiving, 1950.

CLIFFORD S. GARNER

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● CHEMISTRY OF ORGANIC COMPOUNDS

***Carl R. Noller*, Professor of Chemistry, Stanford University. W. B. Saunders Co., Philadelphia, 1951. ix + 885 pp. 97 figs. 28 tables. 16 × 24 cm. $7.**

AS READERS OF THIS JOURNAL will recognize, C. R. Noller has been foremost in advocating application of the molecular orbital theory to the teaching of organic chemistry. Exposition of this theory and a sane use of mechanisms are outstanding features of his text. The fundamental ideas on mechanisms are given in a separate chapter after alcohols and alkyl halides are discussed. Thereafter, mechanisms are presented in fine print.

The order of presentation in this text is neither traditional nor does it follow the presently popular concurrent treatment of aliphatic and aromatic chemistry. After about 400 pages on aliphatic compounds, 250 pages on aromatics and heterocyclics follow and then 200 pages on polyfunctional aliphatic compounds. However, amino acids and carbohydrates are discussed in the first section but the polyfunctional compounds such as acetoacetic ester are given a less prominent position (near the end) than has been customary with most textbook authors. Autoxidation, antioxidants, and organic peroxides, and silicon and phosphorus compounds have been treated at some length, indicating the growing importance of these topics in current thinking. Recent results on mechanisms in peroxide formation is not reviewed, however.

The author must have dug deep to find so many interesting details on industrial processes and the economic aspects of chemistry since these are not easy to find. There are excellent sections on soaps, cellulose products, rubber, and other topics. It is good to see statistics on production for years later than 1940 again.

While the most important name reactions appear, the names themselves are given secondary consideration, a step in the right direction. Since the names are indexed, this causes no undue difficulty in locating them.

Short paragraphs on prominent organic chemists appearing as footnotes present side lights which should provoke students to seek a wider historical background. The men's names are indexed at the end of the book.

The book as a whole is remarkably free of errors of fact and misprints are few.

In appendexes, the Greek alphabet and a guide to pronunciation taken from the *News Edition*, 12, 202 (1934), are given. Inside the back cover is an old short form of the periodic table.

I can find little to criticise adversely in this text; I do not like the order of presentation but that is a matter of taste and the

chapters have cross references so that, after the first few, the order may be chosen.

I have one quarrel with the author on terms and one on punctuation, the first trivial, the second important. In discussing stereoisomerism Noller uses the terms composition, constitution, and configuration. Since the words conformation and/or constellation seem destined to enter the organic chemists' vocabulary, it might be wise to abandon "composition" and "constitution" in favor of words or phrases already adequate. But the second quarrel cannot be dismissed lightly. Repeatedly the author uses the following sentence construction as illustrated by an example taken from page 89: "The great mobility of hydrogen, that is its ease of transfer from one electron-attracting element to another . . . ." While I am not a strict constructionist on punctuation, the sense of this sentence cannot be garnered in one reading unless "that is" is set off by commas. If the Latin signpost "id est" were used then one comma might be considered sufficient since the reader would have warning of what was coming.

LEALLYN B. CLAPP

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● MEDICINAL CHEMISTRY. VOLUME 1

Alfred Burger, **Associate Professor of Chemistry, University of Virginia. Interscience Publishers, Inc., New York, 1951. xviii + 577 pp. 15 figs. 57 tables. 16 × 24 cm. $10.**

VOLUME 1 of this comprehensive treatise contains 28 chapters, to be followed by an additional 15 chapters in Volume 2. The first 6 chapters (72 pages) deal with subjects of a general nature, such as Relation of Chemical Structure and Biological Activity, or Physical Properties and Biological Activity. Beginning with Chapter 7, the reader is introduced to various selected groups of drugs. Descriptions of anesthetics, hypnotics, anticonvulsant drugs, analgetics, analeptics, cardiovascular drugs, and diuretics are followed by a discussion of drugs acting on the gastrointestinal tract, expectorants, adrenergic drugs and blocking agents, parasympathetic stimulants, curare and curariform drugs, and antispasmodics. Chapters on antihistaminic drugs, diagnostic agents, antithyroid drugs, drugs for the treatment of cancer, and vitamins conclude Volume 1.

It is an ambitious enterprise for one person to attempt to cover such a vast field singlehanded. The advantage of having only one author for such a treatise is that a much more uniform, compact, and even treatment of the various subjects is possible than could be hoped for if 28 specialists had collaborated in writing this volume. A disadvantage is—and the author seems to be aware of this—that one individual cannot handle equally well all the aspects of medicinal chemistry. Dr. Burger's research work has dealt mainly with synthetic organic chemistry and his description of the organic chemistry of various drugs is, therefore, authoritative and exact. However, when the author leaves his field of specialization and discusses developments in neighboring sciences his statements are not always equally reliable.

A table on page 19 states that Warburg's respiratory enzyme was found to contain riboflavin. Biochemists call the riboflavin-containing enzymes "yellow enzymes" as differentiated from Warburg's respiratory enzyme or cytochrome oxidase, which contains a hemin-type prosthetic group. On pages 256–7 plasma-accelerator globulin is persistently referred to as globin, which is the protein moiety of hemoglobin. On page 220 it is reported as a fact that chlorophyll absorbs odors and may be taken orally to preclude various body odors. However, the National Bureau of Standards and the National Institute of Health stated in 1944 that chlorophyll was an inert ingredient in a certain household deodorant, and the ineffectiveness of chlorophyll preparations (taken orally) for control of perspiration odors was pointed out recently by Dr. Killian at a meeting of the Society of Cosmetic Chemists.

A statement on page 521 that carboxylase contains five atoms of magnesium fails to consider that only one atom of magnesium per mol of cocarboxylase was found by Kubowitz in Warburg's laboratory. To describe carboxylase (which has the function to split pyruvic acid into acetaldehyde and CO_2) as an enzyme which "transfers phosphoric acid to and from other participants in the carbohydrate cycles, for example adenosine triphosphate" is incorrect. The author apparently confuses this enzyme with other thiamine-pyrophosphate-containing enzyme systems, such as pyruvic acid dehydrogenase. On page 522 structures of a thiol and a disulfide form of thiamine are shown with the statement that these compounds participate in redox systems during the biological utilization of glucose. There are no experimental facts to support such claims.

The reviewer encountered only relatively few misprints in this book; for example: asculatory (page 319) should read auscultatory. The shortcomings mentioned above are not too serious and Dr. Burger's treatise is quite useful to anybody who wishes to have a compact survey of the field of medicinal chemistry.

OTTO SCHALES

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● THE QUANTITATION OF MIXTURES OF HEMOGLOBIN DERIVATIVES BY PHOTOELECTRIC SPECTROPHOTOMETRY

Francis T. Hunter, **Associate in Medicine, Harvard Medical School; Associate Physician and Clinical Pathologist, Massachusetts General Hospital, Boston. Charles C. Thomas, Springfield, Ill., 1951. xx + 226 pp. 6 figs. 44 charts. 16 × 23.5 cm. $8.50.**

THIS small book is directed to biochemists, especially those in medical schools. The specific objective is the popularization of spectrophotometric methods. The illustrative examples are polycomponent systems containing hemoglobin derivatives.

There are essentially two parts to the book, the description and charts. The first half of the descriptive material (Part I, 34 pages) deals with the general principles, including the theory of spectrophotometric measurement of polycomponent systems, and the construction of various kinds of calibration curves and nomographic calculative aids. The remaining descriptive material (Part II, 44 pages) consists of operating directions for determining oxyhemoglobin, hemochromogen, carbon monoxide saturation, oxygen saturation, neutral methemoglobin, hemoglobin pigments in serum, and erythrocyte volume.

Appendices I and II comprise most of the second half of the book, some 100 pages being devoted to transmission curves, simple calibration curves based upon such data, information on the experimental conditions (but without cell thickness), and nomographic aids. All data are for the Cenco-Sheard Spectrophotelometer. Isosbestic is not spelled correctly.

Two ususual usages are the plural form, millimicra, and quantitation for the analyst's word, determination. The reviewer would have preferred closer adherence to the symbols recommended by the Society for Applied Spectroscopy (and other groups). The few references would be more convenient as footnotes on the pages cited. The work of E. S. Miller, F. P. Zscheile, and E. I. Stearns on polycomponent systems might have been mentioned, especially Stearns' use of log log ordinate plotting.

M. G. MELLON

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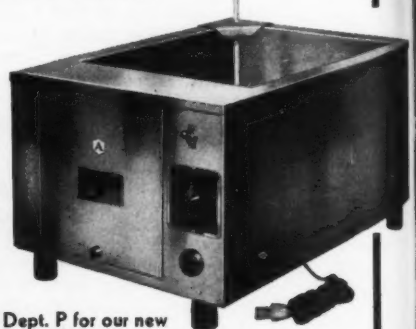

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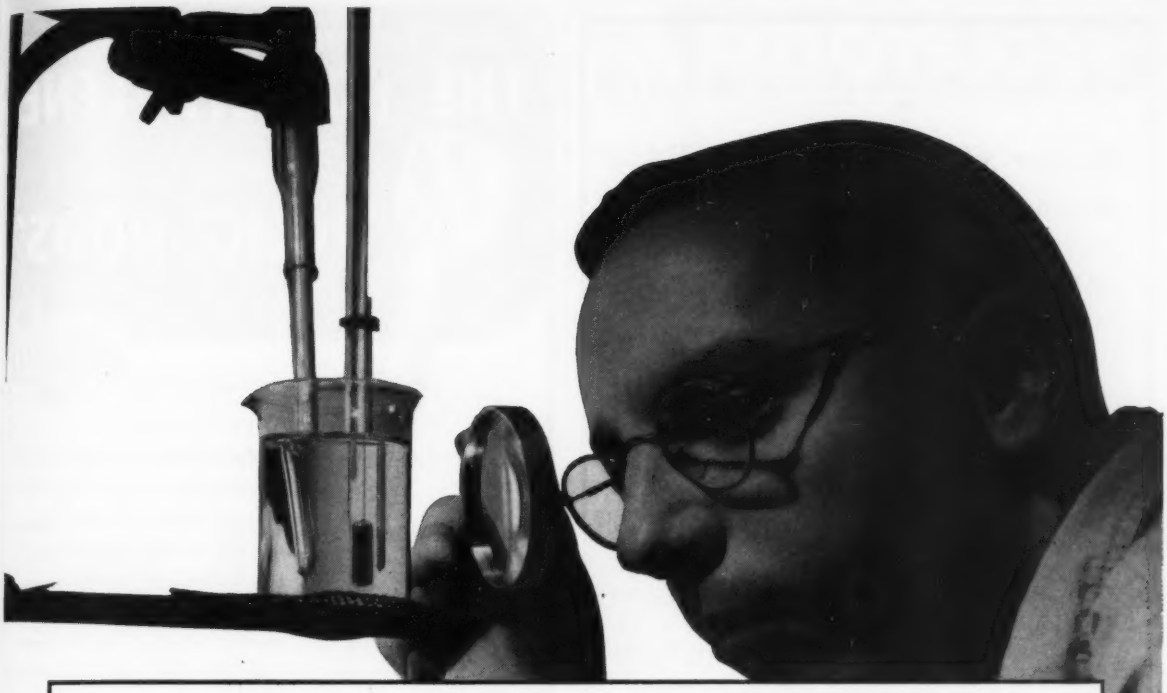

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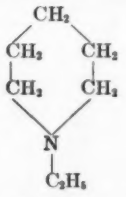

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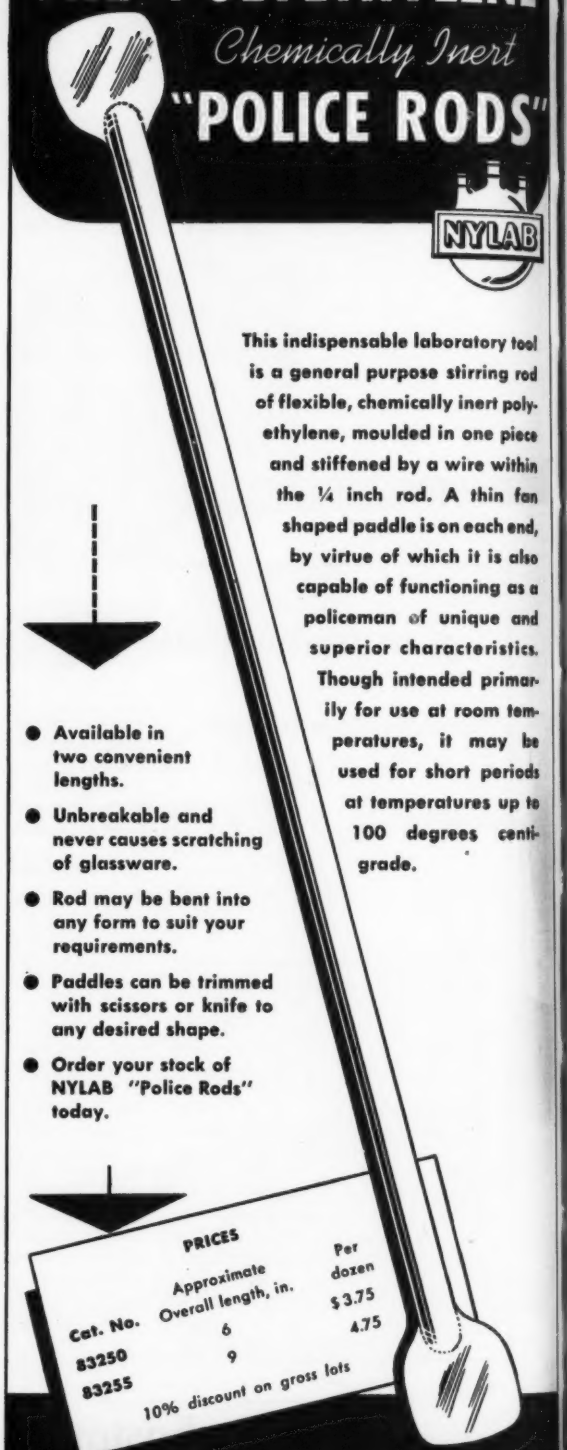

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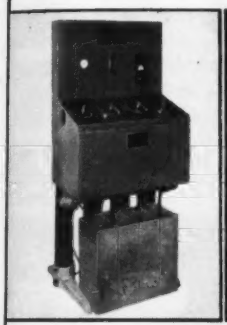

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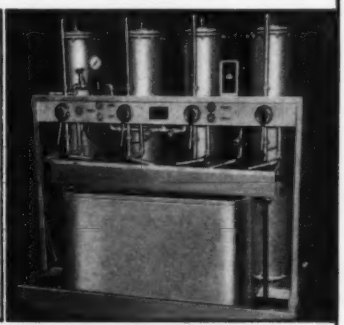

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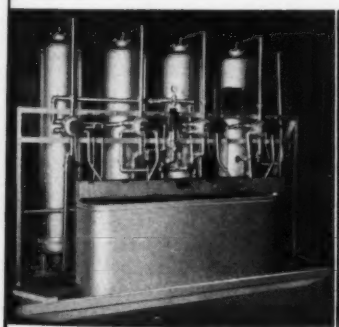

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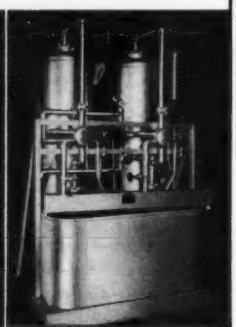

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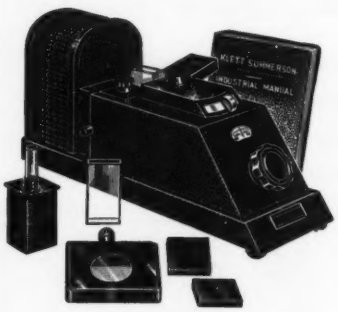

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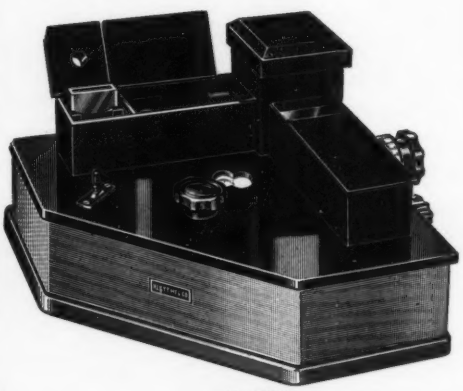

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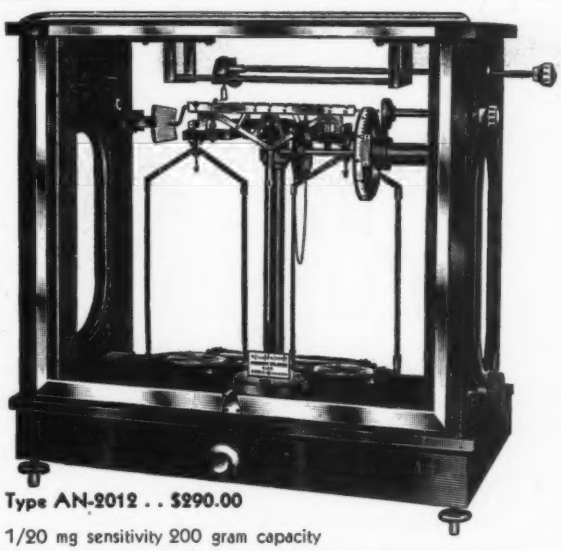

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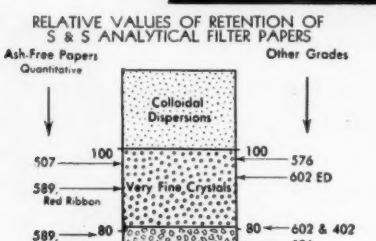

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Instead of peering closely at the thermometer, the operator can take a reading from a distance of 6 ft., and from an angle. A hairline, engraved across the center of the magnifier, can be set at the desired temperature to serve as a reference point.

Color Slides of Atoms

There is available a set of 100 2- × 2-in. color slides, one slide representing the periodic table, 98 representing each atom, and one key slide. Useful for focusing class attention on any one element or group of elements, these slides lend themselves to lecture-room discussion or comparison of the characteristics of the atoms. Further information can be obtained from W. M. Welch Scientific Co., 1515 Sedgwick St., Chicago 10, Ill.

Blotting Paper Test for Water in Alcohol

Small quantities of water in alcohol can be detected merely by putting some alcohol on a specially treated strip of blotting paper. This new and delicate chromatograph test developed by Dr. J. E. C. Stringer of Vickers-Armstrongs, Newcastle-on-Tyne, England, and reported to the journal *Nature*, is expected to determine from one-tenth to one-half per cent of water in alcohol used for chemical purposes.

The alcohol being tested is allowed to soak up through a strip of blotting paper which is impregnated with two chemicals. The alcohol first reaches a zone of iron sulfate, which is dissolved in the water and not in the alcohol. When this salt, picked up by the water, reaches the area containing potassium ferricyanide, a blue coloration consisting of ferric ferrocyanide is produced. The extent and intensity of the coloration depends upon the amount of water present.

pH Indicator

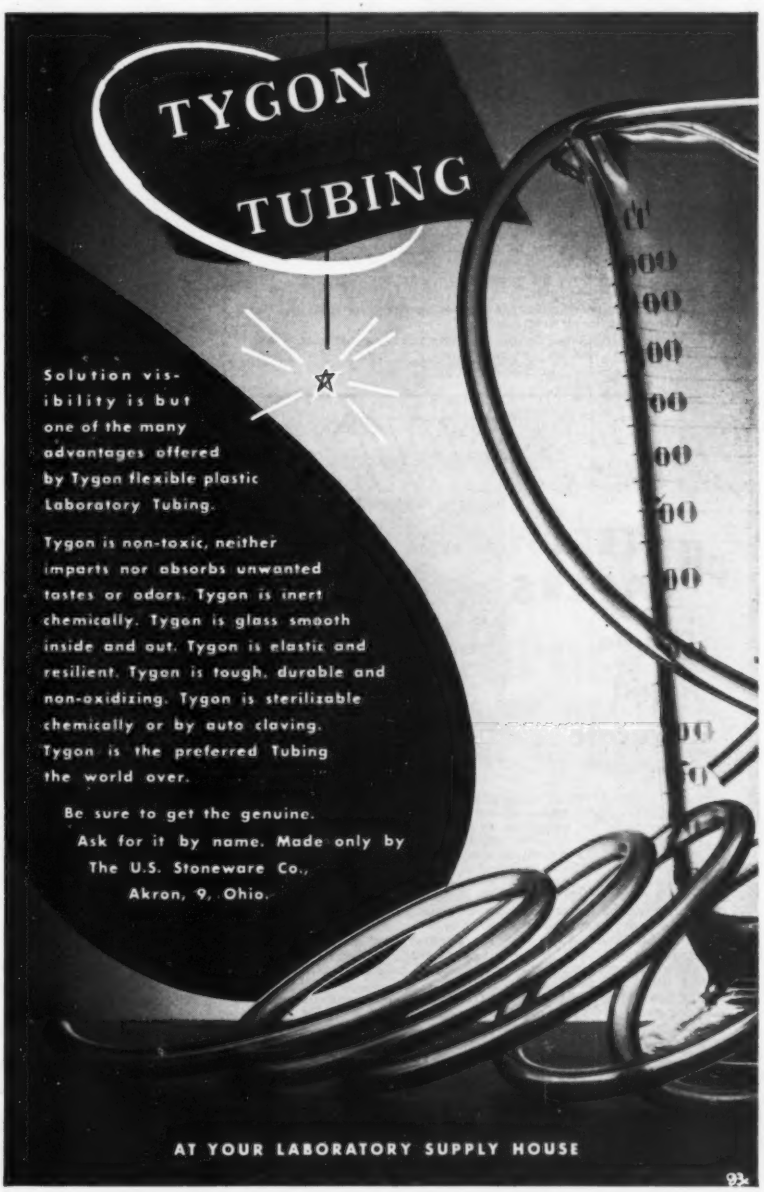
New line-operated pH indicator and vacuum tube voltmeter, developed by Leeds & Northrup, 4934 Stenton Ave., Philadelphia 44, Pa., is unaffected by normal fluctuations in line voltage or by zero drift of the amplifier. A converter-type instrument, its circuit employs d.-c. to a.-c. conversion, a.-c. amplification, and conversion back to d. c. for voltage feedback. Conversion stabilizes zero; feedback stabilizes gain.

Used as a pH indicator, the instrument reads directly in pH; makes glass electrode measurements to within ±0.02 pH on grounded or ungrounded solutions. Continuous pH 0 to 14 scale eliminates range-changing. For manual laboratory use, temperature compensator is graduated from 0° to 100°C. in 2° steps. If the instrument is used as a continuous indicator on industrial process pH, automatic temperature compensation can be provided.

As a vacuum tube voltmeter, the new indicator can be used with any high or low impedance electrode system which develops potentials within range of the instrument. External circuits can have up to 2000 megohms resistance. Current drain does not exceed 1×10^{-12} ampere at null balance. Four additional voltage scales of 0 to +700, 0 to −700, 0 to +1400, and 0 to −1400 millivolts are available for redox, potential, and polarized current measurements.

New Literature

"Laboratory Specials" is the title of a new publication published periodically by Aloe Scientific, a Division of A. S. Aloe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Company, 5655 Kingsbury Street, St. Louis 12, Mo. This attractive brochure contains eight pages of informative material on apparatus and equipment of interest to educational and industrial laboratories.

The November issue of "The Laboratory" published by Schaar & Company, 54 W. Lexington Street, Chicago 7, Ill., contains another interesting article in their series on accidental scientific discoveries. The current number deals with Henri Becquerel's early experiments with uranium ores.

The fall number of "What's New for the Laboratory" has just been published by Scientific Glass Company, 100 Lakewood Terrace, Bloomfield, N. J. Among the new items featured are Teflon-coated ground glass joints, a "self-pumping" still and a flexible Slack Tube Manometer.

New Reagent Catalogue

A new 264-page catalogue of laboratory reagents and fine chemicals is being offered by Baker & Adamson Products, General Chemical Division, Allied Chemical & Dye Corporation.

The catalogue covers more than 1000 high purity chemicals, including such pertinent facts as grades, strengths, maximum limits of impurities, etc., on all reagents.

Extremely useful to the laboratory chemist is a special section dealing with storage and handling chemicals that require extra care. Another informative feature of interest to purchasing, operating, and laboratory personnel is a section on packaging. This contains photographs and full particulars on the major types of packages used by General Chemical for its B&A products in laboratory and bulk quantities.

Copies are available to qualified users and buyers of laboratory and fine chemicals, upon request on business letterhead. Write to Baker & Adamson Products, General Chemical Division, Allied Chemical & Dye Corporation, 40 Rector Street, New York 6, New York.

New Booklet Highlights Various Beckman Instruments

Beckman Instruments, Inc., manufacturers of electrometric pH equipment, spectrophotometers, and other scientific instruments, has recently published a new 16-page booklet which describes and illustrates the important features of some 20 different instruments and basic accessory units featured in the Beckman line of equipment. One section of the booklet is devoted to the various types of Beckman pH meters, glass electrodes, and accessory equipment. Another covers Beckman Spectrophotometric equipment that operates in the visible and ultraviolet ranges, including the Model B, the Model DU, the Flame Attachment units and the Model DUR which permits the continuous automatic analysis of flowing plant streams of either gases or liquids. Still another section describes Beckman Infrared Spectrophotometric equipment, including Model IR-2, Model IR-2T and the new Model IR-3.

Still other sections of the booklet are devoted to such special instruments as the Beckman Automatic Titrator, the Beckman Micro-Microammeter, the Beckman Ultrohmeter, the Beckman Flow Calorimeter, Beckman Radioactivity Instruments, and other advanced equipment that go to make up the complete line of Beckman equipment.

This new booklet—designated as Beckman Bulletin No. 300—is available from the manufacturer—Beckman Instruments, Inc., South Pasadena 36, California.

New pH Indicator Chart

One of the chemical guideposts for a generation of chemists has been the Eastman pH Indicator Chart. On laboratory walls from Boston to Bangkok and Syracuse to Singapore, it has been as much of a fixture—and as frequently referred to—as the laboratory calendar. But now it is about to give way to a new Eastman pH Indicator Chart which is expected, in turn, to prove even more useful than its predecessor.

Showing the hydrogen-ion concentration ranges and color changes of Eastman Indicators, the new chart also gives direction for preparation of the solution. It is available to chemists without charge on request to the Eastman Organic Chemicals Department, Distillation Products Industries, Rochester 3, New York.

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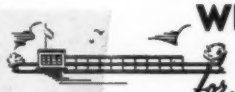

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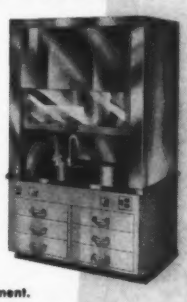

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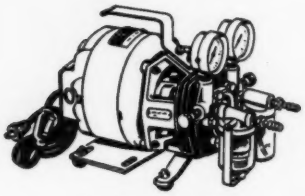

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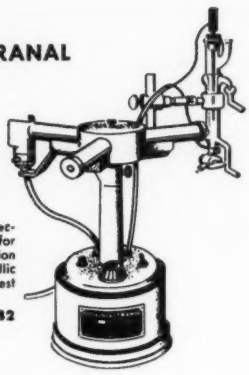

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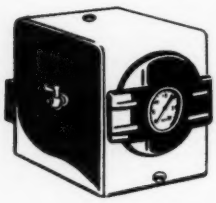

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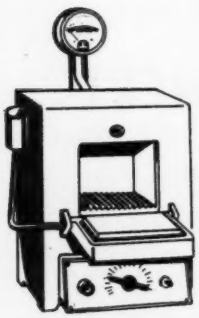

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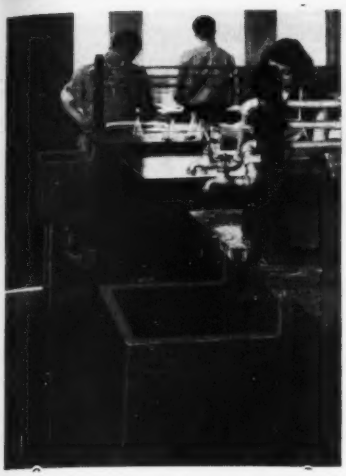

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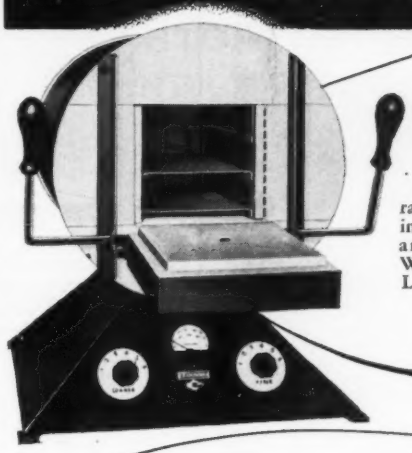

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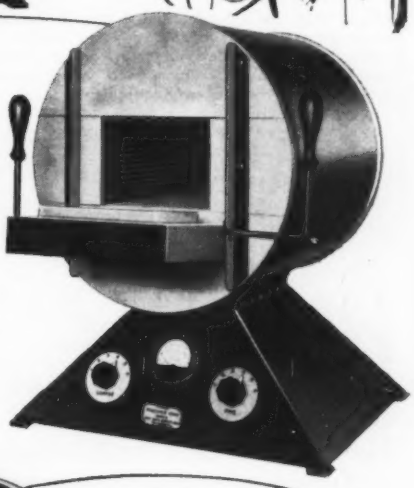

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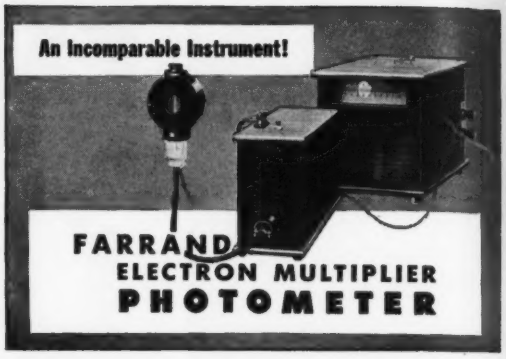

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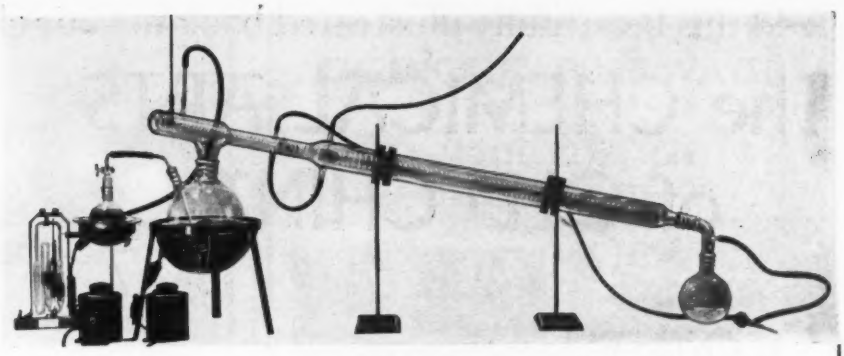

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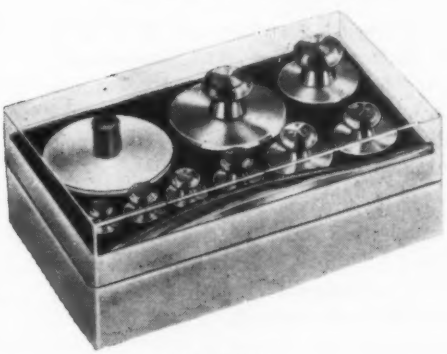

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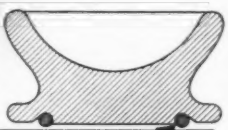

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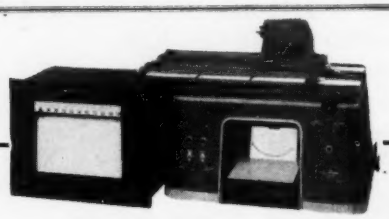

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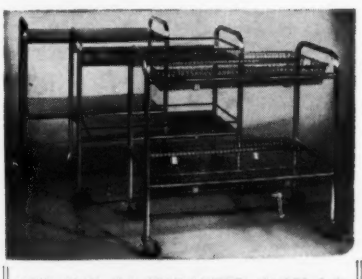

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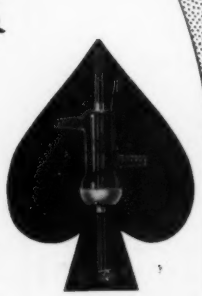

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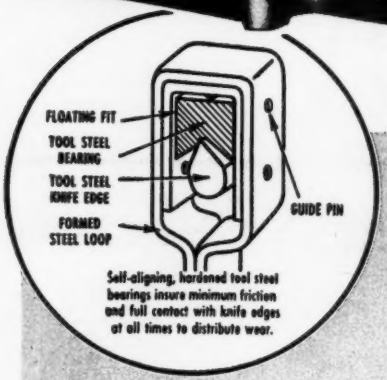
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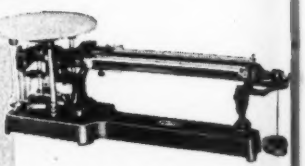

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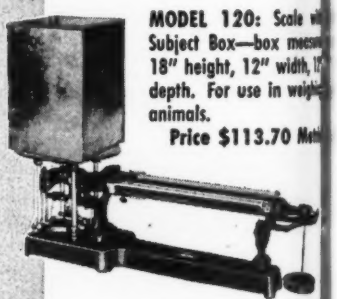

MODEL 120: Scale w Subject Box—box meas 18" height, 12" width, depth. For use in weig animals.
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SPECIFICATIONS

Model	Capac.	Sensitivity	Beam Calibrations Front	Beam Calibrations Back	Undiv. Tare Cap.	Auxiliary Weights	Pan Dia.	Price
119	20 Kg.	1 gram	100 gr. x 1 gr.	1000 gr. x 100 gr.	2270 gr.	10 Kg. x 1 Kg.	11"	$ 93.00
123	45 lbs.	1/16 oz.	2 oz. x 1/16 oz.	2 lbs. x 2 oz.	5 lbs.	20 lb. x 2 lb.	11"	97.50
122	45 lbs.	.002 lb.	.1 lb. x .002 lb.	2 lbs. x .1 lb.	5 lbs.	20 lb. x 2 lb.	11"	101.25
121	20 Kg. or 45 lbs.	1 gram or 1/16 oz.	100 gr x 1gr & 2 oz. x 1/16 oz.	1000 gr. x 100 gr. & 2 lb. x 2 oz.	2270 gr. or 5 lbs.	10 Kg. x 1 Kg. & 20 lb. x 2 lb.	11"	136.50

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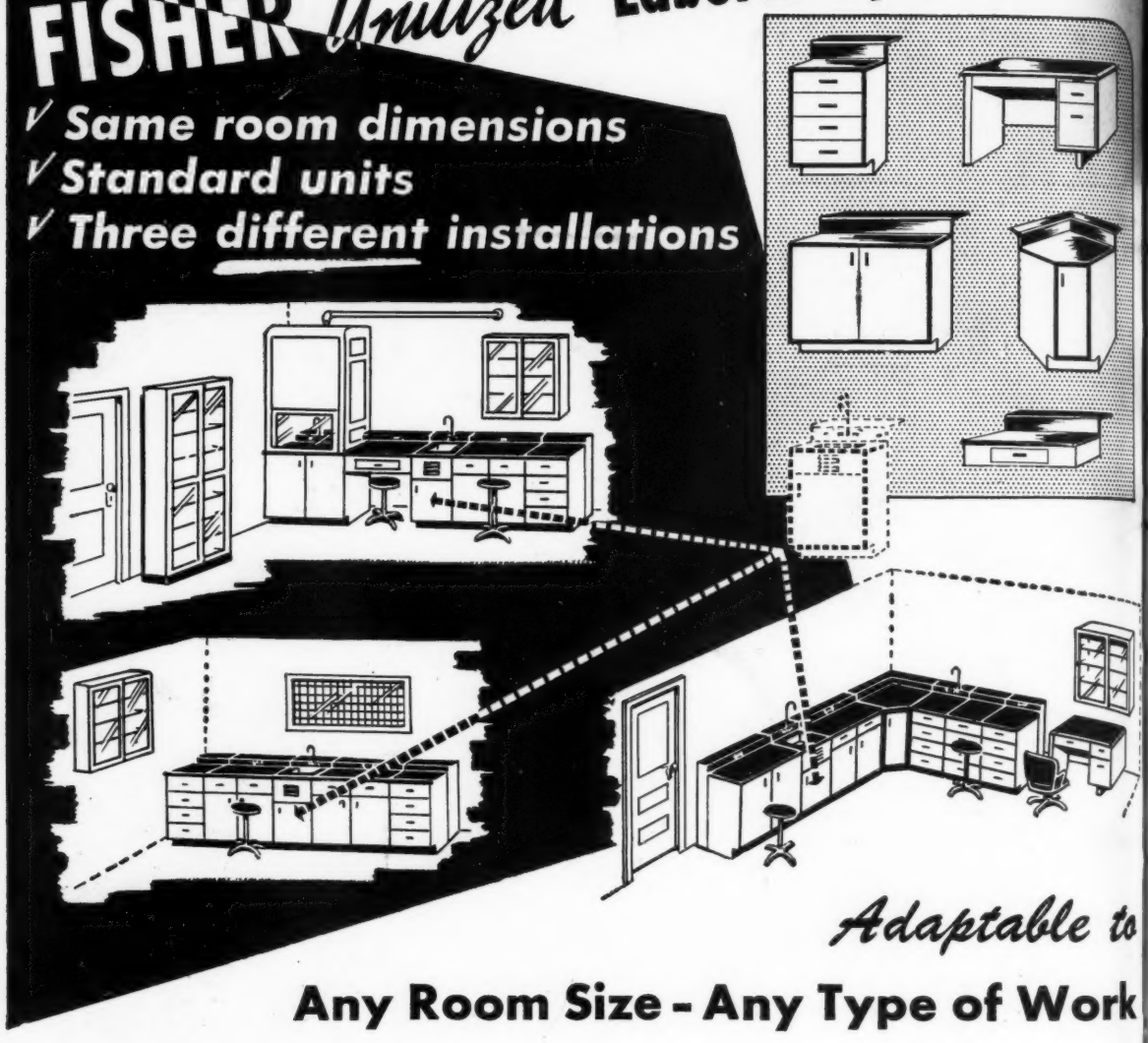

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